Oligocyclopentadienyl Transition Metal Complexes

Cristina G. de Azevedo,*[1] K. Peter C. Vollhardt*
Center for New Directions in Organic Synthesis, Department of Chemistry, University of California at Berkeley and the Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720-1460, USA
Fax: 510 643 5208; E-mail: vollhard@cchem.berkeley.edu

Abstract: Synthesis, characterization, and reactivity studies of oligocyclopentadienyl transition metal complexes, namely those of fulvalene, tercyclopentadienyl, quatercyclopentadienyl, and pentacyclopentadienyl(cyclopentadienyl) are the subject of this account. Thermal-, photo-, and redox chemistries of homo- and heteropolynuclear complexes are described.

Key words: fulvalene, heterodinuclear fulvalene, tercyclopentadienyl, quatercyclopentadienyl, pentacyclopentadienyl.

1. Introduction

The design and construction of "tailored" linked oligocyclopentadienyl (Cp) ring assemblies with defined topology may provide a family of ligands that can function as ideal templates on which to bind metal centers. The reason for the interest in such systems stems in part from the suggestion that polynuclear species may act as suitable models for the interaction of organic

molecules with surfaces[2] and would constitute attractive molecules with which to explore the influence of their rigidly held arrays in organic substrate activation, intrachain ligand migration, electron transfer, and ultimately, synergistic catalysis.

These oligoCp ligands combine: i) the thermodynamic robustness offered by the Cp fragment[3] which is among the most strongly bonded ligands in organometallic chemistry, with bond strengths to metals typically estimated at 90-100 kcal/mol;[3e,f] ii) the fully conjugated nature of the ligand π-system which may permit rapid through ligand electron transfer;[4,5,6] and iii) sufficient proximity of the Cp moieties to allow for adjacent metal-metal bonds.

There are at least two important reasons for the notion that Cp polynuclear systems might exhibit properties quite different from those of their mononuclear (and those not directly attached oligonuclear)[6,7] Cp analogs. First, in the metal-metal bonded configuration, the linked Cp rings are forced to bend away from overall planarity. Indeed, the distance between the ring centroids in a planar bicyclopentadienyl, or fulvalene, linked ligand has been estimated to be about 4 Å,[8] whereas most M-M bonds in fulvalene systems are less than 3.5 Å (Table 1). This bending of the Fv ligand may cause strain which in turn may translate into unique reactivity.[9] Second, the conjugated π system of the Fv ligand provides a mechanism of electronic communication between the metal centers,[9a] regardless of whether there is a metal-metal bond present or not and of whether the metals are oriented cis or trans with respect to the bridging ligand, thus facilitating potential synergism.

Table 1. Some Represenstative M-M Distances (Å) and "Dihedral" Fulvalene Angles, θ (°), in Fulvalenedimetals and Comparison with Selected CpM Dimers

Compound	M-M, Å	θ (°)	Ref.
Fv_2Fe_2	3.984	2.6	10
$[Fv_2V_2(NCMe)_2^{2+}][PF_6^-]_2$	3.329	13.6	11
$FvMo_2(CO)_6$	3.371	15.3	12
$FvW_2(CO)_6$	3.347	16.1	13
$FvRu_2(CO)_4$	2.821	28.5	14a
$FvRu_2(CO)_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}C_2H_2)$	2.719	31.6	14d
$FvCr_2(CO)_6$	3.471	13.0	15
$[CpCr(CO)_3]_2$	3.281	-	16a
$[CpMo(CO)_3]_2$	3.235	-	16b
$[CpW(CO)_3]_2$	3.221	-	16b
$[CpRu(CO)_2]_2$	2.735	-	16c
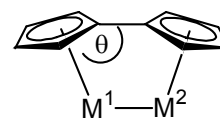
Among the possible oligoCp ligands, it is the simplest fulvalene (Fv) that has attracted most attention and the chemistry of dinuclear organometallic complexes containing this ligand is a topic of continuing interest. The fulvalene system is flexible and can accommodate structures with homo- and heteronuclear metal-metal bonds, additional bridging ligands, cis or trans geometry, sandwich, and cluster arrays,[4,5a,b,6,17] providing complexes with a range of metal-metal distances and different degrees of electronic communication between the metals. Fulvalene complexes also offer the opportunity to compare the properties of analogous mono- and dinuclear Cp-systems in order to test the potential cooperative interaction of two metal centers with a substrate.

About ten years ago, we were stimulated by the emerging rich chemistry of fulvalene complexes[14, 18] to extend the ligand by successive attachment of Cp rings, giving rise to terCp, quaterCp, and higher oligoCp ligands. These can be viewed as cyclopentadienylmetal analogs of the corresponding fulvalene dimetals and as such constitute attractive molecules with which to explore the basic chemical potential of metal arrays rigidly held in "unnatural" configurations.[19] The oligoCp ligands would allow the binding of additional metals and the formation of "super" half-sandwich oligocyclopentadienyl transition metal complexes. At the outset of this work half-sandwich oligoCp complexes were unknown, in contrast to the analogous and extensively investigated sandwich oligometallocenes.[4-6, 20]

This account will provide a selective update on our studies of oligocyclopentadienylmetals, focusing on work accomplished since 1990.[18] Some of the older results are included when it was necessary to provide coherence to the story, but the reader is encouraged to peruse ref. 18 as an introduction. We will begin with the simplest ligand, fulvalene, its attachment to homo- and then heterodinuclear fragments and the chemistry arising from these compounds. We will then move on to the larger systems, comprised of three and four "linearly" linked CpM units and the regio- and stereochemical intricacies associated with their construction. The report ends with the current "record" of our efforts, the assembly of penta(cyclopentadienyl)cyclopentadienylmanganese tricarbonyl. The emphasis throughout will be on the synthetic aspects of the targets.

2. Fulvalene Complexes

2.1. Homonuclear Fulvalene Metal Carbonyls

2.1.1. Synthesis and structural characterization

Our entry into this field occurred in 1983, when it was still in its infancy, with our report[14a,b] of an effective synthetic variant into the class of half-sandwich fulvalene systems. It was based on the discovery that dihydrofulvalene, **1**, is relatively stable when pure and can therefore be converted in the presence of metal carbonyls, "M(CO)" at elevated temperatures to a number of fulvalene homodinuclear compounds (Table 2).
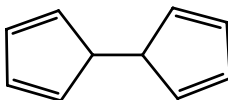
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Table 2. Synthesis of Fulvalenedimetal Complexes from **1**

Complex	"M(CO)"	M	M'	Yield	ref.
FvCo$_2$(CO)$_4$, **2**	Co$_2$(CO)$_8$	Co	Co	80	14b
FvRu$_2$(CO)$_4$, **3**	Ru$_3$(CO)$_{12}$	Ru	Ru	78	14b
FvCr$_2$(CO)$_6$, **4**	Cr(NCEt)$_3$(CO)$_3$	Cr	Cr	71	15^a
FvMo$_2$(CO)$_6$ **5**	Mo(CO)$_6$	Mo	Mo	60	14b
FvW$_2$(CO)$_6$, **6**	W(NCEt)$_3$(CO)$_3$	W	W	72	14b
Fv[Ru(CO)$_2$][Mo(CO)$_3$], **7**	Ru$_3$(CO)$_{12}$ + Mo(CO)$_6$	Ru	Mo	42	14b

^{a} Via fulvalene dianion.

Complexes **2**, **3**, and **5** were prepared by reaction with commercially available $Co_2(CO)_8$, $Ru_3(CO)_{12}$, and $Mo(CO)_6$, respectively. Efficient syntheses of complexes **4** and **6** required the readily accessible propionitrile complexes $Cr(NCEt)_3(CO)_3$ and $W(NCEt)_3(CO)_3$, respectively. The corresponding Cr and W hexacarbonyls are insufficiently labile and the tris(acetonitrile) complexes too insoluble to react with dihydrofulvalene before it polymerizes. Attempts to prepare the iron analog of **3**[21] under these conditions were unsuccessful. The heterodinuclear **7** was the first of its kind.

Most of the fulvalene compounds were found to be more stable than the analogous cyclopentadienyl complexes; they are air stable as solids and oxidize only slowly (over a period of many hours) in solutions protected from light. Their structural characterization (Table 1) shows that they all have a longer metal-metal bond than their Cp analogs. To accommodate such bonds, there is a bend from planarity in the ligand, the "dihedral" angle θ between the two Cp planes generally increasing as the bond length decreases, with a range of 2.6 to 31.6 °.

2.1.2. Reactivity

Of the simple homodinuclear fulvalenes in Tables 1 and 2, the best scrutinized to date are **3**, **5**, and **6**, as described in the following sections. All of these investigations began with the basic aim to establish ligand mobility and substitutional lability under thermal and/or photochemical conditions. Such chemistry is fundamental in the development of new potentially catalytic reactions on the dinuclear frame provided by fulvalene dimetals. A number of surprises were in store for us as these projects got underway, as the systems frequently deviated not only quantitatively, but, more importantly, qualitatively from the known chemistry of their CpM-dimeric relatives.

Homodinuclear Mo and W organometallic zwitterions

Depending on reaction conditions and the electronic and steric properties of PR_3, $Cp_2Mo_2(CO)_6$ may yield phosphine substituted Mo-Mo bonded dimers $Cp_2Mo_2(CO)_{6-x}(PR_3)_x$ (x = 1, 2)[22] or disproportionation products $[CpMo(CO)_2(PR_3)_2]^+[CpMo(CO)_3]^-$.[23] The latter are favored when electron-rich, sterically undemanding, and/or chelating phosphines are used.

8a, M = Mo, L = PMe₃   **8b**, M = Mo
9a, M = W, L = PMe₃   **9b**, M = W
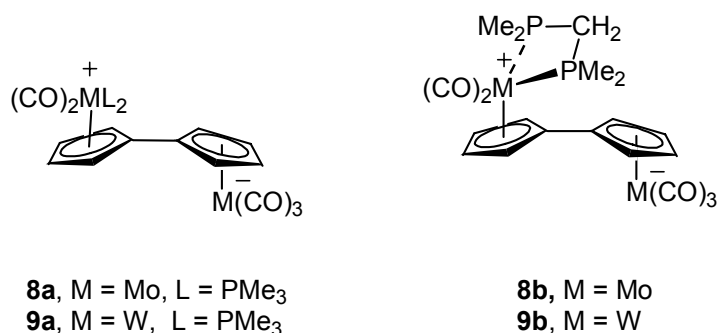
Scheme 1

With this behavior in mind, it was very surprising that treatment of **5** or **6** with PPh_3, $Ph_2PCH_2PPh_2$, or $Ph_2PCH_2CH_2PPh_2$, under thermal or photochemical conditions, gave no isolable products. However, when the reaction was performed with more basic phosphines, such as PMe_3 or $Me_2PCH_2PMe_2$ (dmpm), $FvM_2(CO)_5L_2$ **8a**, **b**, and **9a**, **b** were obtained (Scheme 1).[24]

Complex **8b** was structurally characterized by X-ray diffraction. The molecule consists of two Mo centers bonded to an essentially planar Fv ligand in a trans manner; both rings are planar and the dihedral angle between the two rings is 5 $^{\circ}$. Although conjugated, the molecule prefers the charge localized $\eta^5:\eta^5$-Fv structure rather than the alternative $\eta^6:\eta^4$-Fv form, which would also give each metal 18 valence electrons (Scheme 2). Both $M(CO)_2L_2$(diene)[25] and $M(CO)_3(\eta^6$-fulvene)[26] complexes (L = PR_3; M = Cr, Mo, W) are well known.
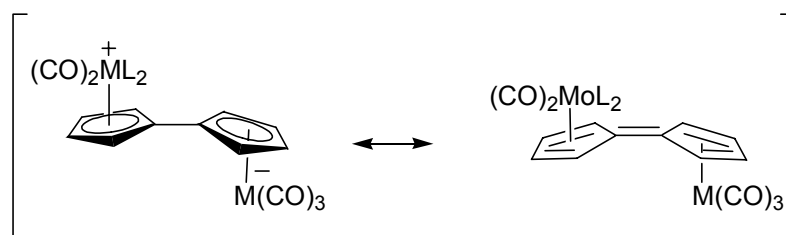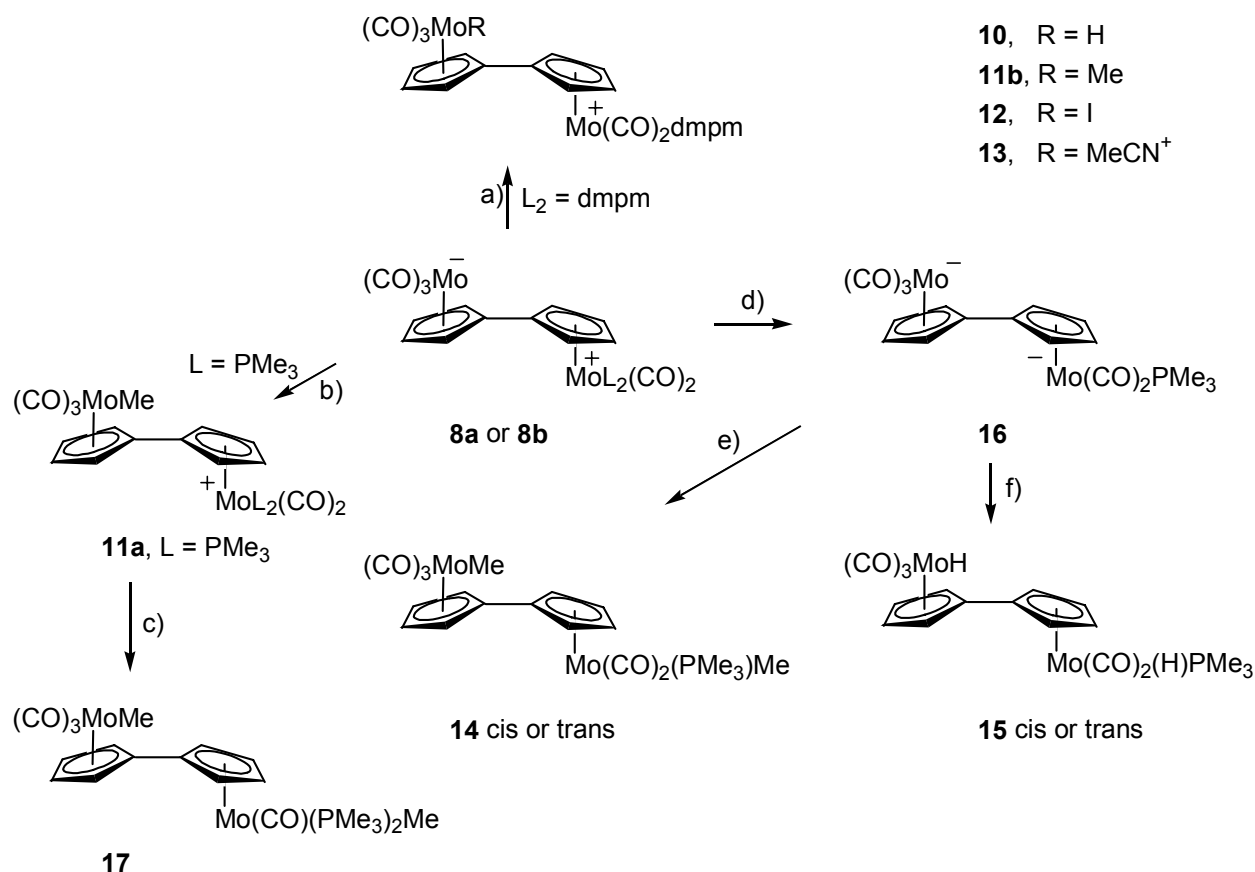

Scheme 2

These two alternatives can be viewed conceptually as either resonance structures or as (rapidly) equilibrating species. The possible contribution (in resonance terms) or availability (when viewed as equilibrating structures) of a fulvalene-diene form is of special importance for the reactivity to be described later. The mechanism proposed for the above reactions is a direct nucleophilic attack of the phosphine that causes heterolytic cleavage of M-M bond to generate a zwitterionic intermediate, as shown in Scheme 3. The relief of strain induced in **5** and **6** by the presence of the bent Fv ligand should enhance such reactivity towards nucleophiles. The cationic half of the resulting intermediate may then undergo substitution by the second phosphine unit to give the final products.
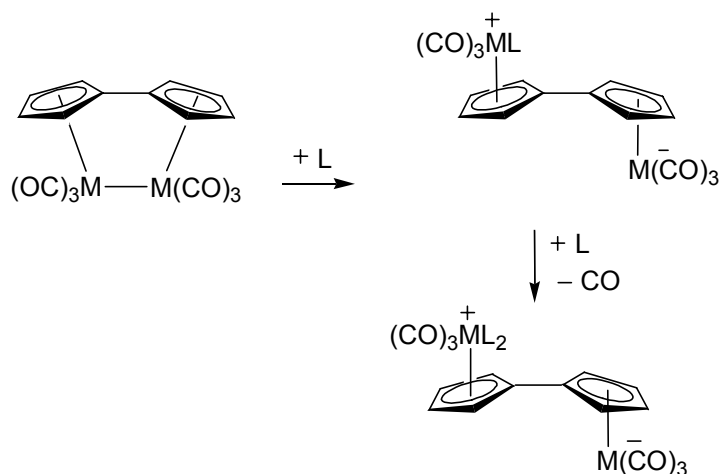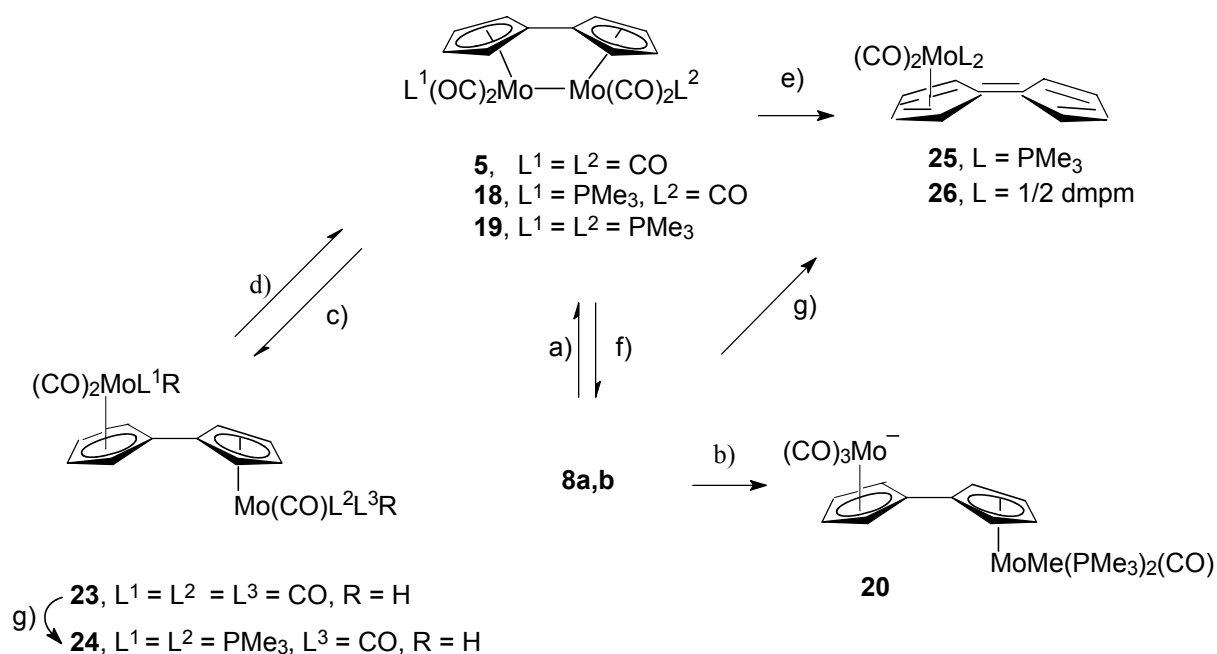

Scheme 3

The chemistry of **8** and **9** is consistent with the dipolar nature of zwitterions which induces dual reactivity: electrophiles add at the anionic end, nucleophiles at the cationic one. Some of the reactions performed are summarized in Scheme 4.

(CO)$_3$MoR

10, R = H
11b, R = Me
12, R = I
13, R = MeCN$^+$

a) L$_2$ = dmpm

(CO)$_3$Mo$^-$

Mo$^+$L$_2$(CO)$_2$

8a or 8b

L = PMe$_3$ b)

(CO)$_3$MoMe

$^+$MoL$_2$(CO)$_2$

11a, L = PMe$_3$

c)

(CO)$_3$MoMe

Mo(CO)(PMe$_3$)$_2$Me

17

d)

(CO)$_3$Mo$^-$

$^-$Mo(CO)$_2$PMe$_3$

16

e)

(CO)$_3$MoMe

Mo(CO)$_2$(PMe$_3$)Me

14 cis or trans

f)

(CO)$_3$MoH

Mo(CO)$_2$(H)PMe$_3$

15 cis or trans

Scheme 4 a) **8b** + HBF$_4$·Et$_2$O → **10**; **8b** + CF$_3$SO$_3$Me → **11b**; **8b** + I$_2$ → **12**; **8b** + AgBF$_4$ → **13**. b) MeI. c) LiAlH$_4$. d) Na/Hg. e) MeI. f) CF$_3$COOH.

Thus, **8b** reacted with HBF$_4$·Et$_2$O, CF$_3$SO$_3$Me, I$_2$, and AgBF$_4$ to afford compounds of general formula [FvMo$_2$(CO)$_5$(dmpm)(R)]$^+$ (R = H, **10**; Me, **11b**; I, **12**; MeCN$^+$, **13**). FvMo$_2$(CO)$_5$(PMe$_3$)$_2$ (**8a**) was unreactive toward NaBH$_4$ (as anticipated on the basis of the reported inertness of [CpMo(CO)$_2$(PPh$_3$)$_2$]$^+$ toward NaBH$_4$[27]) but transformed with LiAlH$_4$ to yield the anion [FvMo$_2$(CO)$_4$(PMe$_3$)$_2$Me]$^-$. A reaction of **8a** with nucleophiles is exemplified by the reduction of coordinated CO to Me, performed by LiAlH$_4$ at the cationic center of FvMo$_2$(CO)$_5$(PMe$_3$)$_2$$^+$ to give FvMo$_2$(CO)$_4$(PMe$_3$)$_2$Me$_2$ (**17**). In analogy to the behavior of FvW$_2$(CO)$_6$H$_2$ (vide infra), irradiation of FvMo$_2$(CO)$_5$(PMe$_3$)H$_2$ (**15**), [and FvMo$_2$(CO)$_4$(PMe$_3$)H$_2$], led to H$_2$ elimination and gave Mo-Mo-bonded complexes FvMo$_2$(CO)$_5$(PMe$_3$) (**18**), [and FvMo$_2$(CO)$_4$(PMe$_3$)$_2$ (**19**)] (Scheme 5).

When treated with an excess of PMe$_3$, **8a** and **8b** underwent surprising decomplexation to form Mo(CO)$_3$(PMe$_3$)$_3$ and FvMo(CO)$_2$L$_2$ (**25**, **26**) in which only one Cp moiety of the Fv ligand was complexed to Mo.

**Scheme 5** a) a. **8a** + Na/Hg, b. CF₃COOH, c. hv → **18**. b) **8a** + LiAlH₄. c) a. **5** + Na/Hg, b. CF₃COOH → **23**. d) **24** + hv → **19**. e) **5** + PMe₃ (excess) → **25**; **5** + dmpm → **26**. f) **5** + PMe₃. g) PMe₃.

No reaction occurred when **19** was treated with an excess of PMe₃, proving that **19** is not an intermediate in the formation of **8a** from **5**. The latter reaction is facile even in the dark, indicating that initial homolysis of the M-M bond is not required. Compounds **25** and **26** can be made directly from **5** by demetallation, a process that can be reversed by the addition of metal carbonyls. The former constituted the first examples of ring slippage in a fulvalene system and opened up the way to a designed synthesis of heterodinuclear complexes (Section 2.2.1.). Spectral data indicated a geometry reflecting both contributing resonance forms **27** and **28** (Scheme 6). Evidence in support of the structure proposed was provided by the X-ray structural analysis of the Ru analog, obtained upon treatment of **3** with a large excess of PMe₃.[14d]
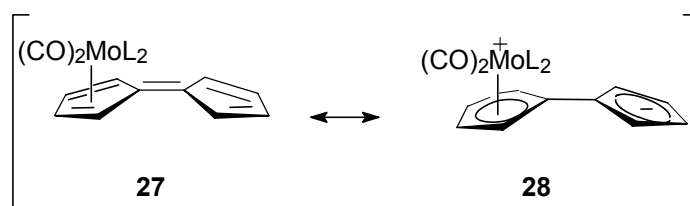
Scheme 6

The reactions between **8a,b** and PMe₃ came as a surprise, since the anionic site should not be expected to react with PMe₃ for electronic reasons and the cationic site should be rendered unreactive for steric reasons. A possible mechanism[24a] is depicted in Scheme 7 and involves hapticity changes in **8a** that render it subject to nucleophilic attack.   When exposed to Mo(CO)₃(NCMe)₃, FvMo(CO)₂(PMe₃)₂ (**25**) cleanly regenerated FvMo₂(CO)₅(PMe₃)₂ (**8a**).

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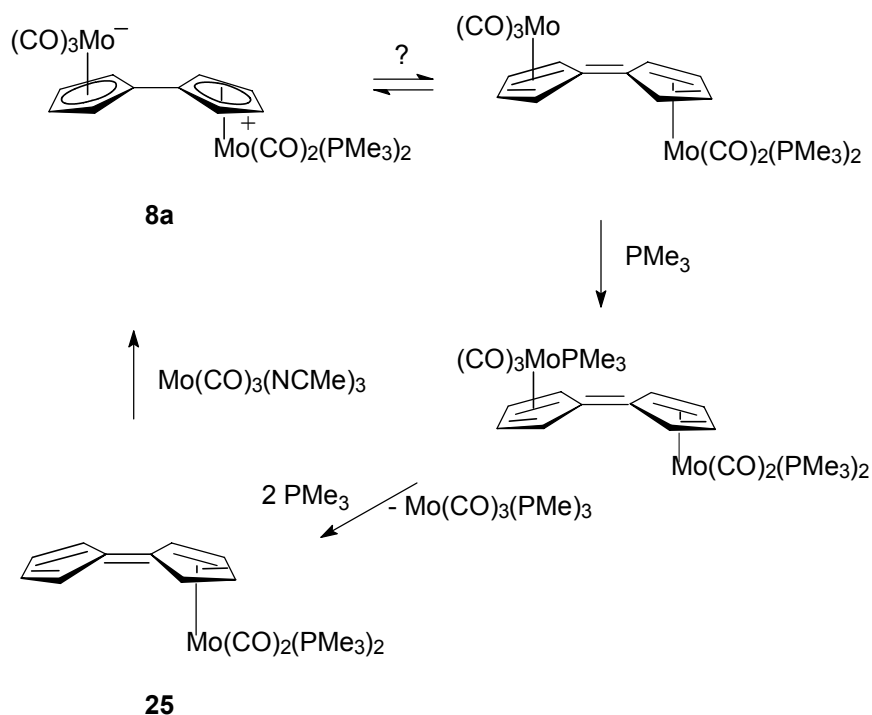
Scheme 7

Photo- and thermal reactivity of FvM₂(CO)₆, M = Mo, W

Photolysis of FvMo$_2$(CO)$_6$ (**5**) in the presence of alkynes afforded mono- and bis(alkyne) complexes FvMo$_2$(CO)$_4$(RC≡CR) **30-32** and FvMo$_2$(CO)$_3$(RC≡CR)$_2$ **33** and **34**, respectively, as in Scheme 8. Spectroscopic evidence indicated that the former bears as a ligand a μ-η^2-alkyne and that this ligand is mobile around the Mo-Mo bond in a rapid fluxional process.[12]

30, R = H
31, R = Ph
32, R = CO$_2$Me

33, R = Ph
34, R = CO$_2$Me
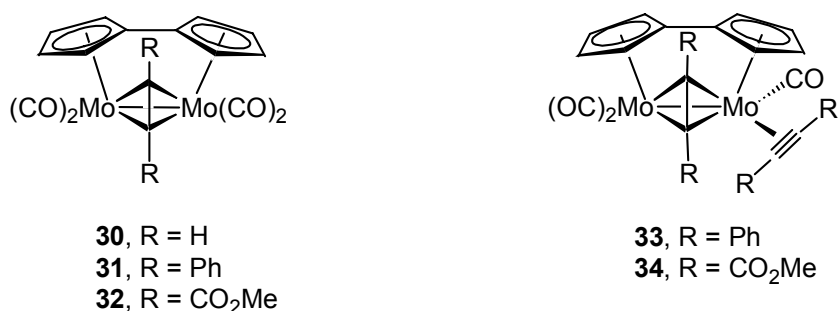
Scheme 8

The bis(alkyne) systems contained uncoupled alkynes, as determined by an X-ray diffraction study of **34**. This result is unusual in light of the frequent occurrence of alkyne coupling at a binuclear center.[28] Several unsuccessful attempts were made to induce such coupling in **33** and **34**. It is difficult to find a rationale for this departure from the chemistry of the analogous Cp compounds. Perhaps a bridging metallacycle requires a relatively short metal-metal distance, which might be prevented in **33** and **34** by the resulting strain energy in the fulvalene ligand.

These results should be compared to those obtained in the photochemical reactions of FvW$_2$(CO)$_6$ (**6**) with alkynes.[29] Here, single and double alkyne photosubstitution was also observed in the presence of diphenylethyne to afford complexes **35** and **36**, whose structures were proposed based on spectroscopic data (Scheme 9). It is interesting to note that in **35** the alkyne functions as a 2e ligand, stopping short of conversion to the 4e ligand system analogous to **30-32**.
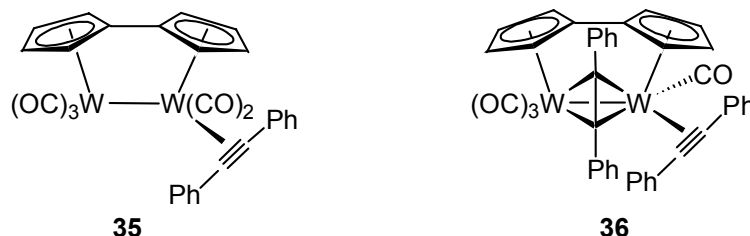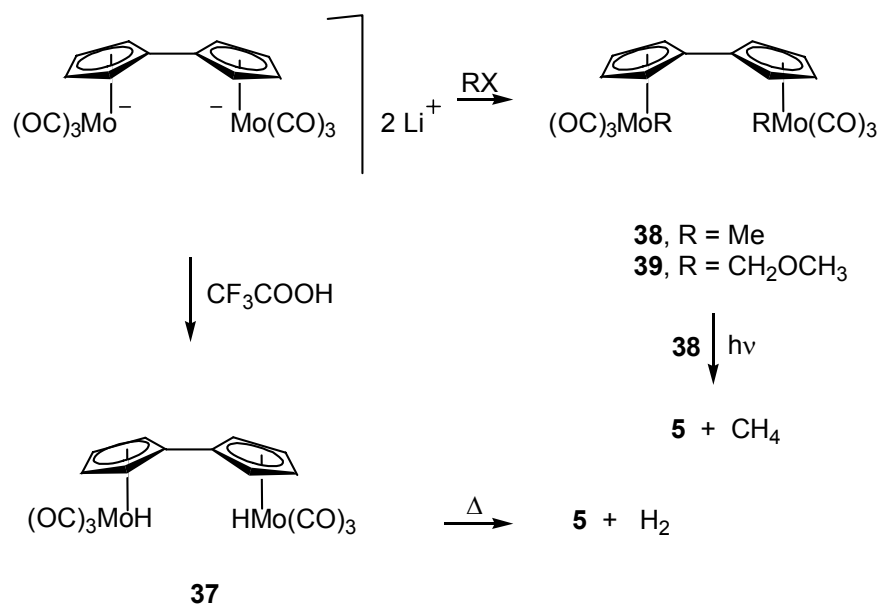

Scheme 9

In related work, in collaboration with Amouri´s group in Paris, the complex formed from **5** and MeC≡CCH$_2$OMe, FvMo$_2$(CO)$_4$(μ,η^2-η^2-MeC≡CCH$_2$OMe), afforded on protonation the carbenium ion [FvMo$_2$(CO)$_4$(μ,η^2-η^3-MeC≡CCH$_2$)]BF$_4$ in which the fluxional process of the alkyne ligand already noted in the systems **30-32** is superimposed on another involving reversible complexation of the cationic center to either metal.[30]

Formation of dihydride, dialkyl, and carbene complexes from the dianions [FvM$_2$(CO)$_6$]$^{2-}$, M = Mo, W

The metal-metal bonded complexes FvM$_2$(CO)$_6$ (M = Cr, Mo, W) undergo facile two-electron electrochemical reductive cleavage of the metal-metal bonds (vide infra). This result suggested that a dianion should be readily accessible from **5** and provide a useful starting material for further functionalization as already indicated in Scheme 5. Indeed, the reported procedure for preparing Na[Cp(CO)$_3$Mo] from Cp$_2$Mo$_2$(CO)$_6$ and Na/Hg[31] was applied to the synthesis of the dianion [FvMo$_2$(CO)$_6$]$^{2-}$[Na$^+$]$_2$, and the dilithium salt was conveniently prepared from lithium triethylborohydride. These species are rapidly air-oxidized to **5**. Li$_2$[FvMo$_2$(CO)$_6$] was protonated instantaneously by trifluoroacetic acid in THF at 20°C to give the dihydride FvMo$_2$(CO)$_6$H$_2$, **37** (Scheme 10). It underwent ready intramolecular elimination of dihydrogen, a reaction of interest as a model for the desorption of H$_2$ from metal surfaces.

Addition of primary alkyl, allyl, and benzyl halides to [Cp(CO)$_3$Mo]$^-$ has been known to afford the corresponding substituted compounds CpMo(CO)$_3$R.[31] Not surprisingly, subjecting Li$_2$[FvMo$_2$(CO)$_6$] to various haloalkanes produced the alkylated derivatives FvMo$_2$(CO)$_6$R$_2$. In analogy to the methyl complex Cp(CO)$_3$MoMe,[35a,b] FvMo$_2$(CO)$_6$(Me)$_2$ (**38**) was observed to decompose photochemically to yield **5** and large quantities of methane (Scheme 10). On the basis of labeling experiments, it appears that the departing methyl group abstracts hydrogen from the cyclopentadienyl ring. The mechanism of H$_2$ evolution from **37** may follow that proposed for the corresponding Cr analog[9b] involving both metals (as suggested by kinetic experiments), but was not conclusively established.

Scheme 10

Treatment of Fv(Mo)$_2$(CO)$_6$(CH$_2$OMe)$_2$ (**39**) with HBF$_4$·Et$_2$O at -20 ℃ (CD$_2$Cl$_2$) produced FvMo$_2$(CO)$_6$(CH$_2$OMe)(=CH$_2$)$^+$ (**40**), as determined by NMR spectroscopy. Warming to 0 ℃ gave the carbene-coupling product FvMo$_2$(CO)$_6$(C$_2$H$_4$)$^{2+}$, **42**, (Scheme 11). The possible intermediate bis(carbene) FvMo$_2$(CO)$_6$(=CH$_2$)$_2^{2+}$ (**41**) was not detected. Compound **42** decomposed on further warming with the evolution of ethene. The sequence in Scheme 11 can be viewed as a binuclear model for carbene coupling on surfaces.[2]
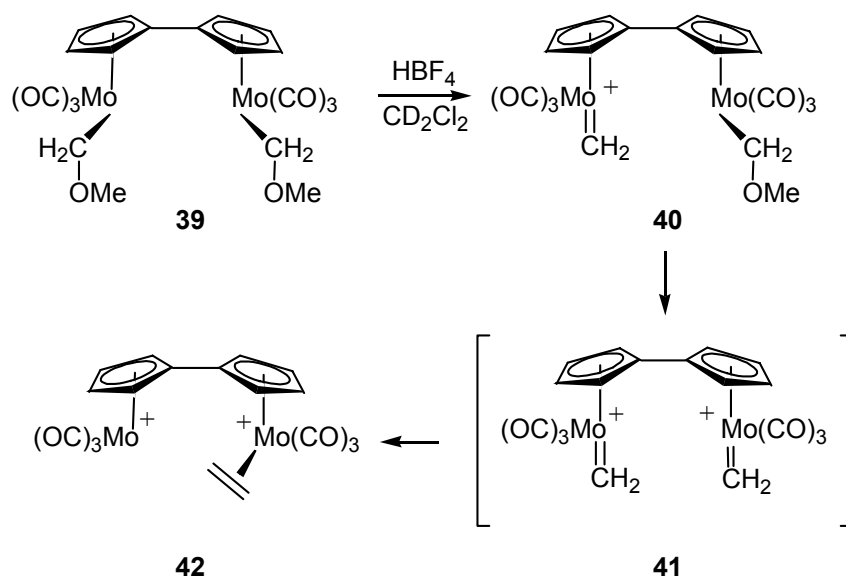
Scheme 11

The facile alkylations depicted in Scheme 11 suggested that it might be possible to synthesize the novel dimetallacycles of the type **43** by the reaction of [FvMo$_2$(CO)$_6^{2-}$] with dihaloalkanes. To our delight, instead, exposure to I(CH$_2$)$_3$I gave a metal-metal bonded 1-oxacyclopent-2-

ylidene complex, **44** (Scheme 12). An X-ray diffraction analysis showed that the Fischer-type carbene ligand was terminally bound. However, this complex exhibited fluxional behavior via a bridging carbene species, the first such process observed. Thermolysis (100 ºC) led to efficient generation of propene and **5** by an unprecedent retro-ene reaction on a dinuclear matrix.[12]
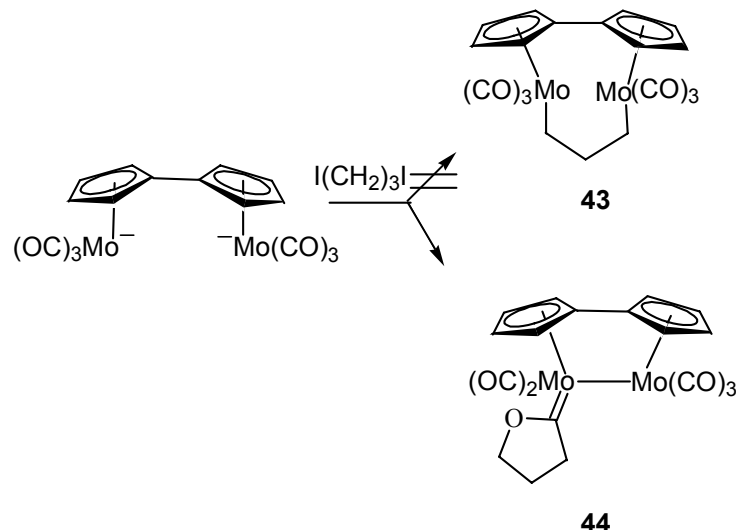
Scheme 12

As its Mo analog, $FvW_2(CO)_6$ (**6**) underwent reduction by $LiEt_3BH$ or Na/Hg to form the Li^+ and Na^+ salts of the corresponding dianion. An X-ray crystallographic analysis of $[Et_4N]_2[FvW_2(CO)_6]$ showed it to contain a planar Fv ring system bonded to the two metal centers in trans fashion,[24a] as observed in analogous FvM_2 systems lacking M-M bonds[5a,9b,12,17f,h,32,33] (with the exception of those endowed with addition M-M bridges).[34] $[FvW_2(CO)_6]^{2-}$ exhibited chemistry that is similar to but also occasionally quite different from that of the Mo relative. Thus, it attacked a number of electrophiles to yield the neutral disubstituted compounds $FvW_2(CO)_6R_2$ (R = H, Me, Et, CH_2OMe, σ-C_3H_5, CH_2Ph).

Photolysis of $FvW_2(CO)_6Me_2$ yielded methane gas and $FvW_2(CO)_6$.[24a] This reactivity parallels that of $FvMo_2(CO)_6Me_2$ (Scheme 10),[12] $CpMo(CO)_3Me$,[35] and $CpW(CO)_3Me$.[35] The source of the fourth H (necessary for CH_4) in the W system is a second methyl group, and it differs, in a puzzling way, from that for $FvMo_2(CO)_6Me_2$ and $CpMo(CO)_3Me$ (the source of the hydrogen being mostly the ring systems) and $CpW(CO)_3Me$ (solvent).

In contrast to Scheme 12, $FvW_2(CO)_6^{2-}$ and 1,3-iodopropane provided only the bis(3-iodopropyl) complex, $FvW_2(CO)_6(CH_2CH_2CH_2I)_2$. The absence of Fischer-type carbenes in the case of the W compound may be due to less facile CO insertion into W-alkyl bonds. On the other hand, the W analog of **39**, upon treatment with $HBF_4 \cdot Et_2O$, reproduced the chemistry depicted in Scheme 11.[24a]

The dihydride complexes $FvM_2(CO)_6H_2$ (M = Cr, Mo, W) are plausible, although not observed, intermediates in the reactions of metal carbonyl precursors with dihydrofulvalene to provide the corresponding metal-metal-bonded complexes $FvM_2(CO)_6$ (Table 2).[9b,14b,15] $FvCr_2(CO)_6H_2$ and $FvMo_2(CO)_6H_2$ could be prepared from the corresponding dianions by protonation and were

indeed readily decomposed to **4** and **5**, respectively, and H_2 at 20 °C.[9b,12] On the other hand (and as expected for W), the dihydride **45** turned out to be considerably more stable and therefore subject of further investigation.[24a] Its ^1H NMR spectrum established the presence of two terminal hydride ligands. This notion was also supported by its reactions with CCl_4, $CHBr_3$, and I_2 to yield the corresponding dihalide complexes (Scheme 13).
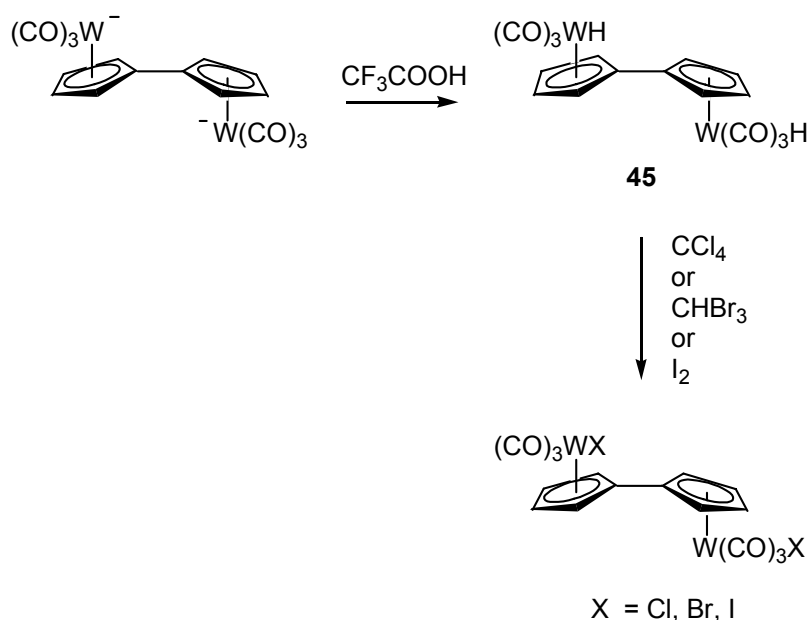
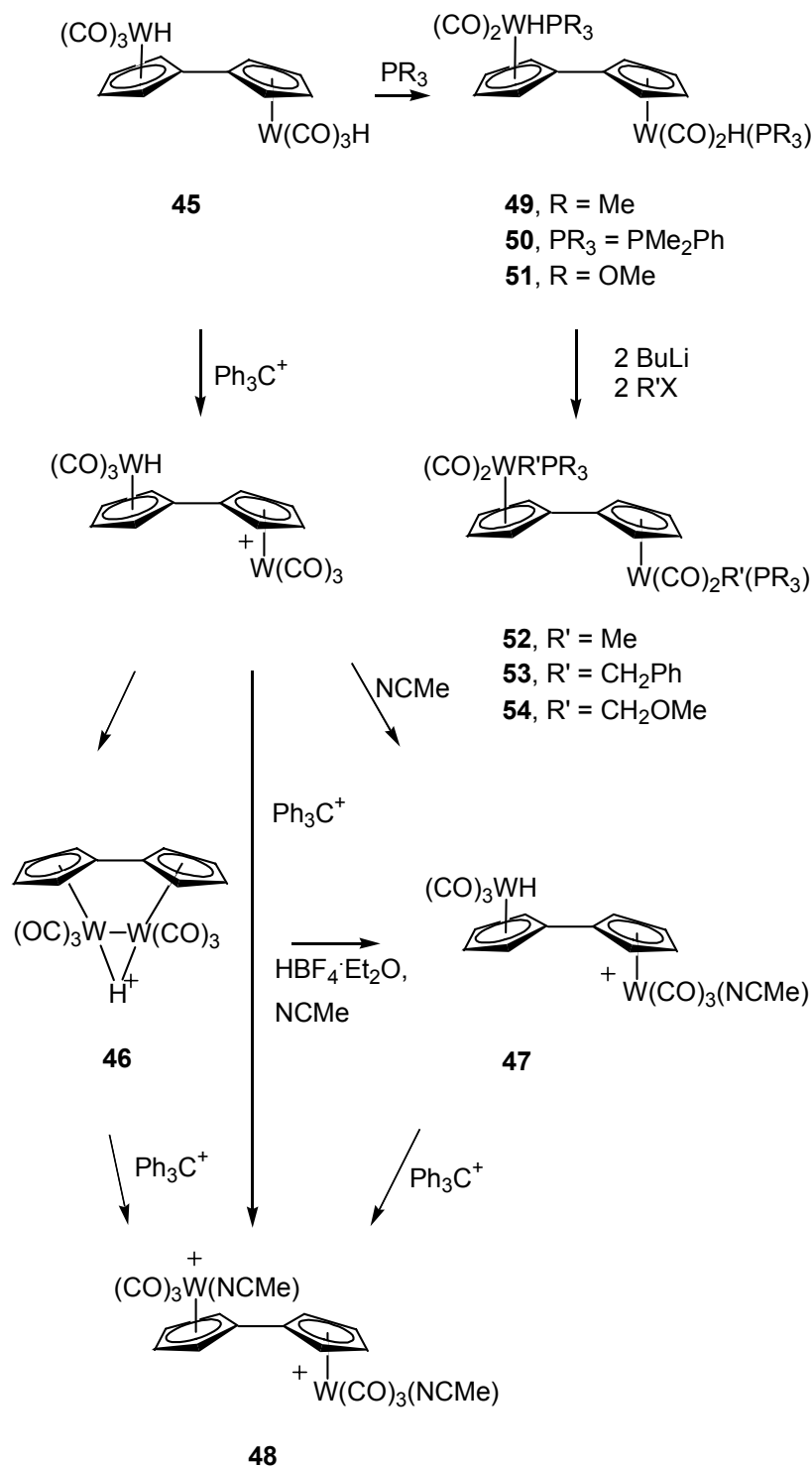**Scheme 13**

The pK_a values for the two consecutive deprotonations of **45** were determined as 14.0 and 16.6 by equilibrium measurements in acetonitrile. Thermolysis (and photolysis) yielded $FvW_2(CO)_6$ (**6**) and H_2. Kinetic measurements in ether solvents suggested the intervention of a radical chain, perhaps obviating a concerted binuclear elimination reaction under these conditions.[9b] Pure **45** was inert with respect to H_2 elimination on the time scale and at the temperature that is employed for the synthesis of **6** from dihydrofulvalene and $W(CO)_3(NCEt)_3$. Under the latter conditions, however, it is likely that radical initiators are present that may well facilitate the extrusion of H_2. The questions posed by these results are now being addressed by more detailed studies of the hydrogenation of **5** and **6**.

Unlike $Cp_2W_2(CO)_6$, $FvW_2(CO)_6$ (**6**) underwent protonation of the W-W bond by $HBF_4 \cdot Et_2O$ in acetonitrile to the bridging hydride $[FvW_2(CO)_6(\mu\text{-}H)]^+$ (**46**). The W-W bond in $FvW_2(CO)_6$ appears therefore more basic than that of $Cp_2W_2(CO)_6$, perhaps due to the strain energy contained in **6**. However, there are other factors that may contribute to the basicity of Fv(M-M) bonds and this result cannot be generalized.[9b,36]

The studies concerning cationic complexes derived from $FvW_2(CO)_6$ and the dihydride $FvW_2(CO)_6H_2$ are summarized in Scheme 14.[24a] Treatment of **46** with excess of $HBF_4 \cdot Et_2O$ in CD_3CN afforded the monohydride $[FvW_2(CO)_6(H)(NCCD_3)]^+$ (**47**). Double hydride abstraction from $FvW_2(CO)_6H_2$ occurred instantaneously when 2 equiv. of Ph_3CPF_6 were added, yielding $[FvW_2(CO)_6(NCMe)_2][PF_6]_2$ (**48**). This product was also accessible from the bridging dihydride **46** and 1 equiv. of Ph_3C^+. The removal of the hydride from **46** (with a great H^+ character) as H^-

(CO)$_3$WH

PR$_3$

(CO)$_2$WHPR$_3$

W(CO)$_3$H

W(CO)$_2$H(PR$_3$)

45

49, R = Me
50, PR$_3$ = PMe$_2$Ph
51, R = OMe

Ph$_3$C$^+$

2 BuLi
2 R'X

(CO)$_3$WH

$^+$ W(CO)$_3$

(CO)$_2$WR'PR$_3$

W(CO)$_2$R'(PR$_3$)

52, R' = Me
53, R' = CH$_2$Ph
54, R' = CH$_2$OMe

NCMe

Ph$_3$C$^+$

(OC)$_3$W—W(CO)$_3$

H$^+$

46

(CO)$_3$WH

$^+$ W(CO)$_3$(NCMe)

HBF$_4$·Et$_2$O,
NCMe

47

Ph$_3$C$^+$

Ph$_3$C$^+$

$^+$
(CO)$_3$W(NCMe)

$^+$ W(CO)$_3$(NCMe)

48

Scheme 14

by Ph$_3$C$^+$, requires an electronic rearrangement in the molecule, which can be one of the reasons for the high kinetic barrier observed. Simultaneously, the electrostatic repulsion between the two cationic reagents does not favor the reaction.[37]

Although, as already pointed out (Scheme 1), the M-M bonded FvM$_2$(CO)$_6$ species (M = Mo,[12] W[22]) are less prone to enter into thermal or photochemical substitution reactions by phosphines

than are their $Cp_2M_2(CO)_6$ analogs, the dihydride **45** underwent ready substitution of CO for phosphines, affording **49**, **50**, and **51** in a near 1:1 mixture of cis and trans configurations at the metal centers. Deprotonation of these species, followed by dialkylation, gave the corresponding dialkyl complexes **52-54** (Scheme 14).

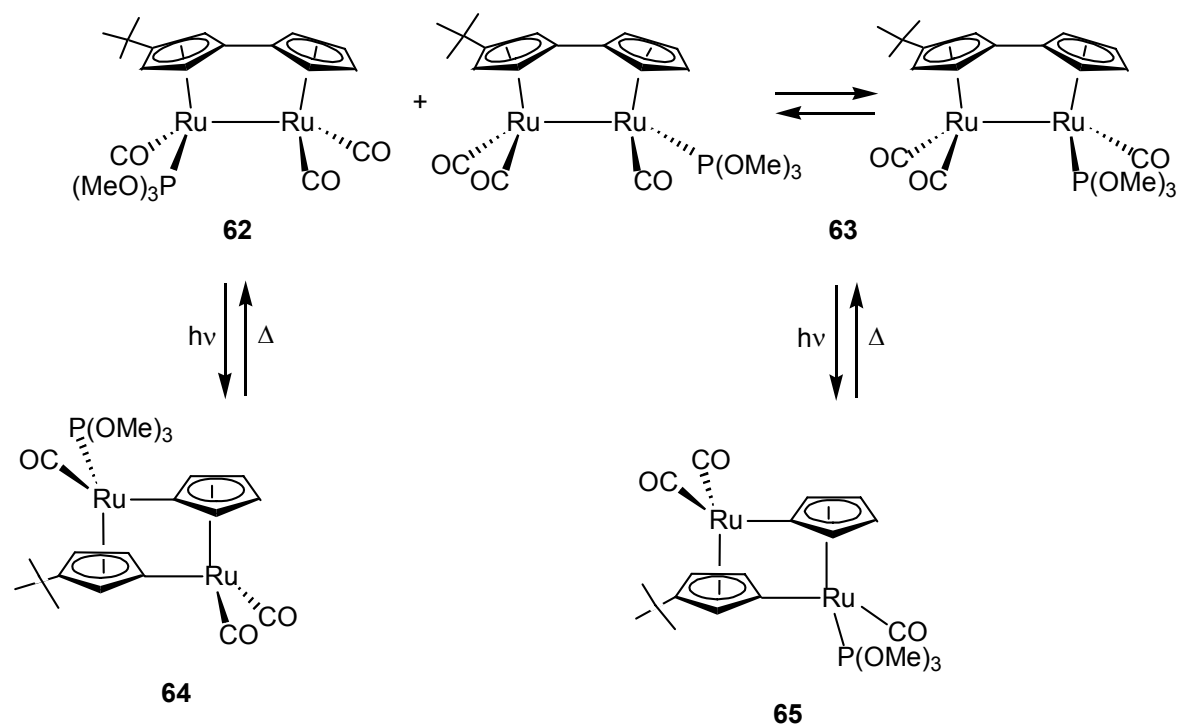### *Thermally reversible photoisomerization of $FvRu_2(CO)_4$*

Like its Cp analog $[CpRu(CO)_2]_2$,[38] $FvRu_2(CO)_4$ (**3**) is fairly inert to thermal ligand substitution. In contrast to the Cp-metal dimer, which undergoes CO loss and metal-metal bond homolysis upon irradiation,[39] photolysis of **3** (350 nm or sun light) led to the formation of the complex $(\mu_2\text{-}\eta^1{:}\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4$ (**55**).[14a,40] An X-ray structural determination of the latter revealed that both the Ru-Ru bond and the central C-C bond in the Fv ligand of **3** had been cleaved and that a remarkable binuclear oxidative addition to a C_{sp2}-C_{sp2} bond had occurred (Scheme 15). A number of $\mu^2\text{-}\eta^1{:}\eta^5$-Cp complexes are known, mostly derived by (formal) C-H activation of a metal bound η^5-Cp unit.[32a,40,41] For **55**, this moiety was generated by insertion of a bimetallic fragment into a C-C bond, a rare transformation.[42] The quantum yield for this process (0.15) was unaffected by the presence of CCl_4, and chlorinated products were not detected. The "electronic window" for successful photoisomerization is narrow, as **59** and **60** (prepared from **3** and the respective phosphine at 120 ºC) did not enter this pathway, nor do any other FvM_2 complexes. However, **61** (to give **56**) and fulvalene substituted derivatives of **3** and **61** were similarly reactive. In the presence of alkynes, **3** or **55** (or a mixture of the two) eventually underwent photosubstitution of CO to furnish the new (for FvM_2) bridging alkyne complexes **57**. Loss of CO was also effected by higher energy UV light (300 nm) which transformed **3** (**55**) into cluster **58**, topologically readily derived from **3** and **55** by formal decarbonylative coupling.

Equally remarkable to the photoprocess **3** → **55** was the finding of clean thermal reversal (> 65 C°) **55** → **3** (and **56** → **61**) with the release of 29.8 kcal mol^{-1} of energy. Thus, the system constitutes a relatively efficient and energy rich light energy storage cycle. The conversion of $\mu^2\text{-}\eta^1{:}\eta^5$-Cp complexes to fulvalene dimetals has precedence in the literature.[40,43]

3

57

55, L = CO
56, L = P(OMe)$_3$

59, L = PEt$_3$
60, L = PMe$_3$
61, L = P(OMe)$_3$

58
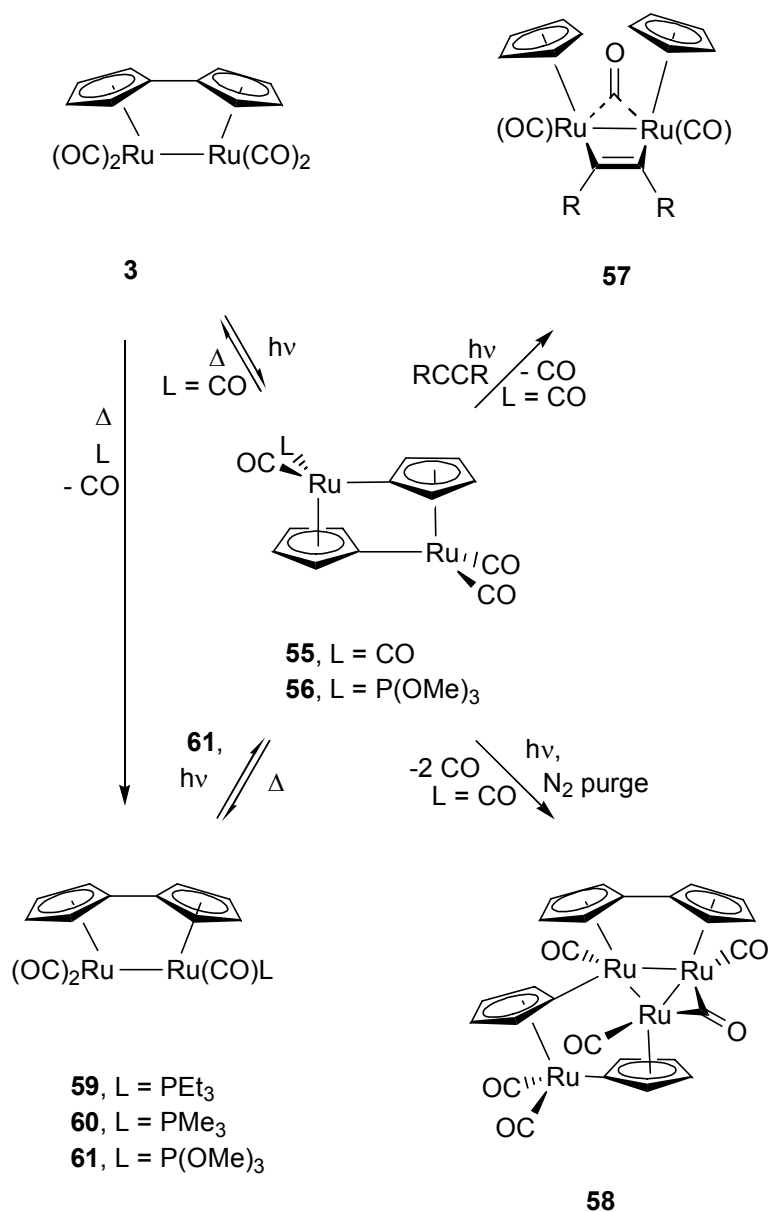
Scheme 15

An extensive series of mechanistic experiments was executed. Thus, a crossover experiment involving **3** and **3**-d_8, in conjunction with clean first order kinetics for the thermal reversal of **55**, pinpointed the intramolecular character of these isomerization. Moreover, using P(OMe)$_3$ as a means to label one of the Ru atoms and *tert*-butyl as a stereo-and regiomarker of the Fv moiety showed that the basic connectivity of the FvM$_2$ core stayed intact during the photochemical-thermal sequence (as, for example, in Scheme 16). All of the evidence points to concerted mechanisms, as shown in Scheme 17, presumably involving different electronic states (ground state versus excited state) for the individual species in the manifold, and analogous to those proposed by Green for the molybdenocene dimer manifold **66** ⇌ **67**.[43,44]

62   **63**

64

65

Scheme 16

3,   M = Ru, L^1 = L^2 = CO
66, M = Mo, L^1 = Cp, L^2 = H

55, M = Ru, L^1 = L^2 = CO
67, M = Mo, L^1 = Cp, L^2 = H
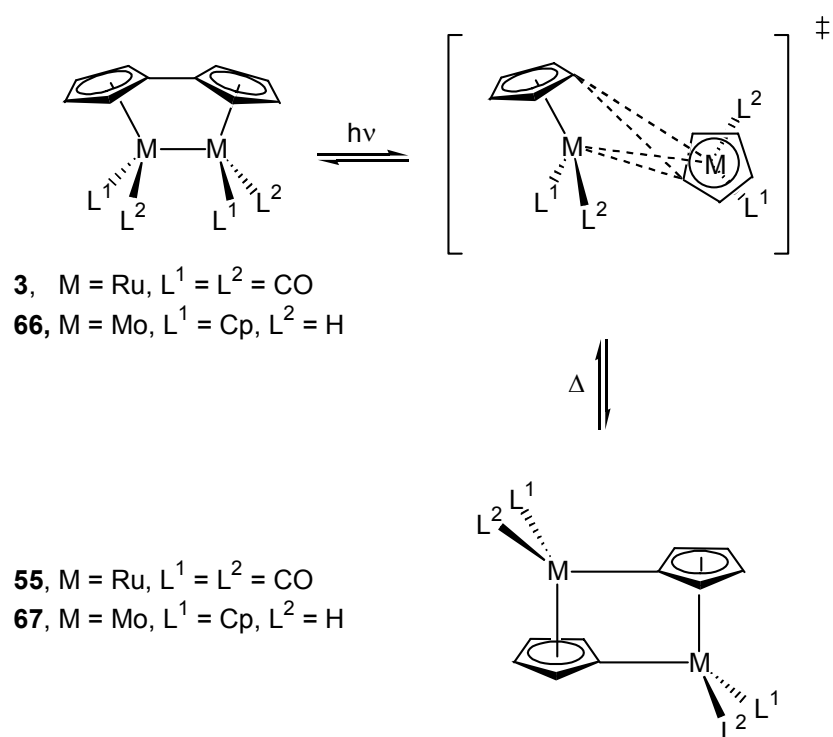
Scheme 17

2.1.3. Conclusions

The resemblance between Cp and Fv ligands often produces similar chemistry, for example, in substitution reactions, which is not surprising considering the analogous microenvironment around the individual metal centers. Numerous ligand substitution reactions and functional group manipulations that are typical of Cp-bonded metal centers can be faithfully reproduced at the two metal centers that are attached to the Fv ligand. However, there are also qualitative and quantitative differences in reactivity, and these are, of course, the ones for which we were looking.

For example, the pK_a measurements showed that the metal hydride acidities decreased in the order FvW$_2$(CO)$_6$H$_2$ (14.0) > CpW(CO)$_3$H (16.1) > [FvW$_2$(CO)$_6$H]$^-$ (16.6). The acidity of the metal hydride, located between that of FvW$_2$(CO)$_6$H$_2$ and [FvW$_2$(CO)$_6$H]$^-$, shows that there is electronic communication between the two metal centers, through the Fv ligand.

The metal-metal bond cleavage reactions of FvM$_2$(CO)$_6$ (M = Mo, W) leading to the respective zwitterionic species seem to be facilitated by the relief of strain of the Fv ligand. The decomplexation reactions observed for the zwitterionic compounds are favored by the capacity of the Fv ligand system to undergo gradual ring slippage to accommodate reduced hapticity bonding modes; this versatility is not available for a mono Cp ligand. Similar strain arguments can be made for the relative ease of protonation of FvW$_2$(CO)$_6$. Conversely, increased strain may be responsible for the relative reluctance of FvM$_2$ to support alkyne couplings to tightly bridging metallacycles. On the other hand, the observation of bridging alkynes **57**, contrasting the bonding pattern in **35**, points to subtle stereoelectronic effects that still need to be unraveled.

Most striking is the unprecedented photo- and thermal chemistry of FvRu$_2$(CO)$_4$ in which both the electronic and structural peculiarities of the molecular frame, albeit still not completely understood, must play a fundamental role.

2.2. Heterodinuclear Fulvalene Metal Complexes

Heterometallic clusters elicit great fascination, because of the presence of potentially uniquely reactive polar M-M bonds and the possibility of synergistic or, at least, cooperative activation of separate functionalities and reagents.[45] It is therefore not surprising that we were interested in the Fv variety of such systems from the very beginning of our studies,[14b] an effort that went hand in hand with the development of ever simpler methods to construct the Cp-Cp bond to provide chemoselective access to such systems. The inherent synthetic challenge has been appreciated by others.[46]

2.2.1 Synthesis

We have reported[47] three synthetic strategies for the construction of heterobimetallic fulvalene complexes. The first is based on the remetallation of the previously described monometallic ring slippage products **25** and **68** of FvMo$_2$(CO)$_6$ (Scheme 5) and FvRu$_2$(CO)$_4$, respectively, and has

the Fv ligand already in place.[47a] The second utilizes a stepwise assembly of the Fv frame, exploiting the nucleophilic property of Cp anion to attach a masked Cp ring.[47a,b] The third and most direct approach makes use of the discovery that Cp anion (as such or in stannylated form) undergoes Pd catalyzed coupling with readily available[48] iodocyclopentadienylmetal complexes.[47c]

Scheme 18 exemplifies the first approach giving rise to a number of novel heterodinuclear organometallic zwitterions. The addition of $M(CO)_3(NCMe)_3$ (M = Cr, Mo, W) to a THF solution of **25** or **68** gave the mixed metal complexes **8a** and **69-72** in essentially quantitative yields.[47a] Metal-metal bonded molybdenum-iron and -zirconium complexes **73** and **74** were obtained by reduction of **25** followed by the addition of the respective transition metal chlorides. The "slipped" approach to $Fv[Ru(CO)_2][Mo(CO)_3]$ (Table 2) provided a high yielding entry into this system, and this route afforded also the mixed metal complexes of Ru-Fe (**75**) and the early-late metal combination Ru-Ti (**76**).[49]

$(CO)_xM^1(PMe_3)_2$

$\xrightarrow{M^2(CO)_3(NCMe)_3}$

$[(CO)_3M^2]^-$

$^+M^1(CO)_x(PMe_3)_2$
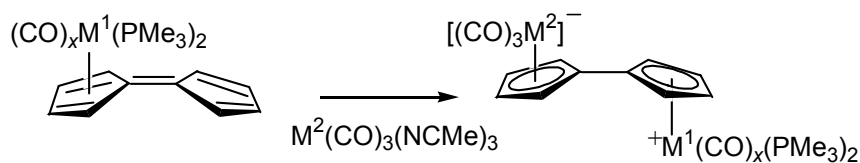
25, M^1 = Mo, x = 2
68, M^1 = Ru, x = 1

8a, $M^1 = M^2$ = Mo, x = 2
69, M^1 = Mo, M^2 = Cr, x = 2
70, M^1 = Ru, M^2 = Cr, x = 1
71, M^1 = Ru, M^2 = Mo, x =1
72, M^1 = Ru, M^2 = W, x = 1

25 $\xrightarrow{Na/Hg}$

$\xrightarrow{Fe(CO)_4Br}$ $(OC)_2Fe\!-\!Mo(CO)_2PMe_3$

73

$\xrightarrow{Cp^*ZrCl_3}$ $Cp^*(Cl)Zr\!-\!Mo(CO)_2PMe_3$

74

68

$\xrightarrow[2.\ Na/Hg]{1.\ Fe(CO)_5}$ $(CO)_2Fe^-$ $^+Ru(CO)(PMe_3)_2$

75

$\xrightarrow{CpTiCl_3}$ $CpCl_2Ti$ $^+Ru(CO)(PMe_3)_2Cl^-$

76
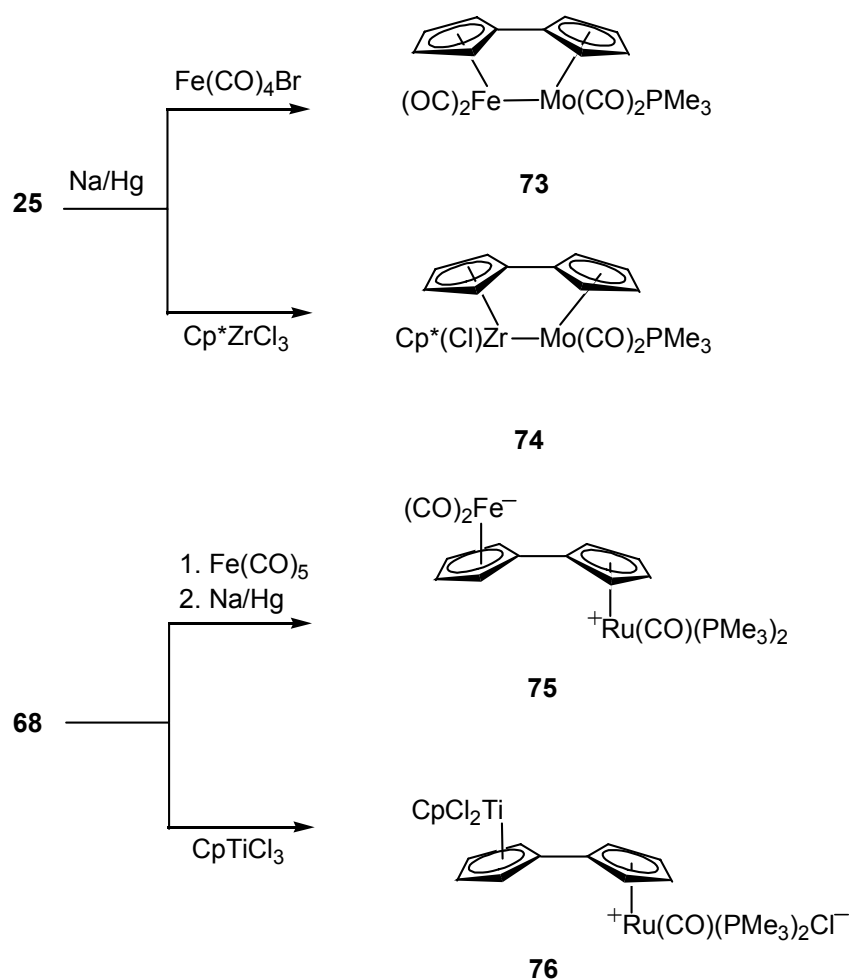
Scheme 18

The second strategy to heterodinuclear fulvalene systems took advantage of purely organic synthetic methodology to append a 3-oxo-1-cyclopentenyl unit to Cp anion. In the first generation of the execution of this route, a cumbersome stepwise sequence was employed, which consisted of reaction of Cp anion with dimethyl butanedioate, one carbon homologation of the resulting keto ester, metallation of the Cp, and intramolecular aldol condensation to give **78** or **79** in 10 and 13% overall yield, respectively.[47a] A tremendous boost in efficiency was realized

when we discovered that Cp anion underwent Michael addition-elimination to 3-alkoxy- (or 3-halo-) cyclopentenones to furnish the enolate **77** quantitatively (Scheme 19). The latter could then be treated with a metalating reagent to introduce a (first) metal into the eventual Fv frame selectively. Elaboration of the cyclopentenone substituent to give the second Cp unit was accomplished by reduction with LiAlH$_4$, followed by catalytic dehydration with p-toluenesulfonic acid, giving cyclopentadiene complexes of the type **80** and **81**.

78, M = Mo
79, M = W

80, M = Mo
81, M = W
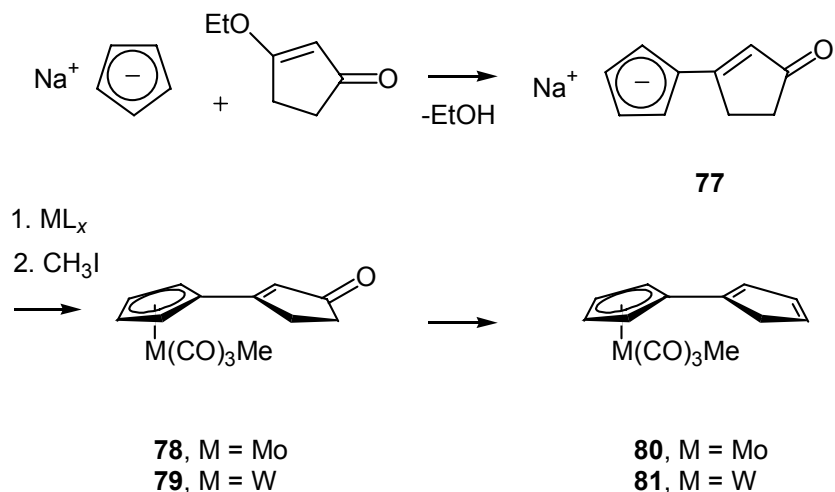
Scheme 19

Their versatility is illustrated for **81** by the preparation of a variety of heterobimetallic complexes, both with or without metal-metal bonds (Scheme 20).[47b] Cyclopentadiene complex **80** presents a parallel chemistry.[50]

81

1. NaH
2. [ML$_n$]X

M(CO)$_x$

Co$_2$(CO)$_8$ or
V(CO)$_6$

82-88

89-92

93, 94
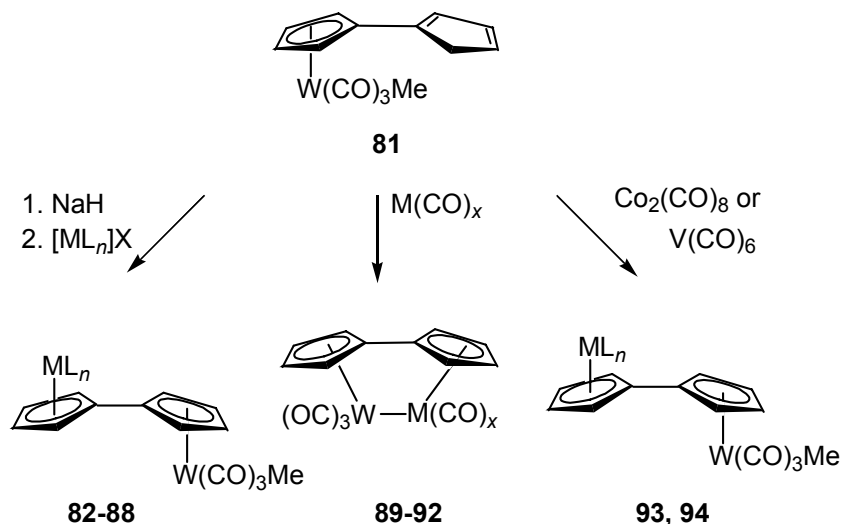
Reagent	ML_n	Compound	Yield (%)
$[Rh(CO)_2Cl]_2$	$Rh(CO)_2$	**82**	73
$[Rh(C_2H_4)_2Cl]_2$	$Rh(C_2H_4)_2$	**83**	64
$Ir(CO)_3Cl$	$Ir(CO)_2$	**84**	25
$[Mn(CO)_4Br]_2$	$Mn(CO)_3$	**85**	71
$Re(CO)_3(THF)Br]_2$	$Re(CO)_3$	**86**	64
$Mo(CO)_3(MeCN)_3$, MeI	$Mo(CO)_3Me$	**87**	44
$Cp*ZrCl_3$	$Cp*ZrCl_2$	**88**	20
$Fe(CO)_5$	$Fe(CO)_2$	**89**	68
$Ru_3(CO)_{12}$	$Ru(CO)_2$	**90**	46
$Mo(CO)_3(MeCN)_3$	$Mo(CO)_3$	**91**	39
$Cr(CO)_3(MeCN)_3$	$Cr(CO)_3$	**92**	48
$Co_2(CO)_8$	$Co(CO)_2$	**93**	63
$V(CO)_6$	$V(CO)_4$	**94**	30

Scheme 20

A third and latest approach is the most direct and is based on the discovery that Heck type coupling of trialkylstannylcyclopentadienes with iodocyclopentadienylmetals[48] occurs readily[47c] to generate **81** (89%) and the corresponding $Mn(CO)_3$ (61%) and $Fe(CO)_2CH_3$ (50%) analogs. This method appears to be quite general and a particularly powerful application is presented in Section 5.
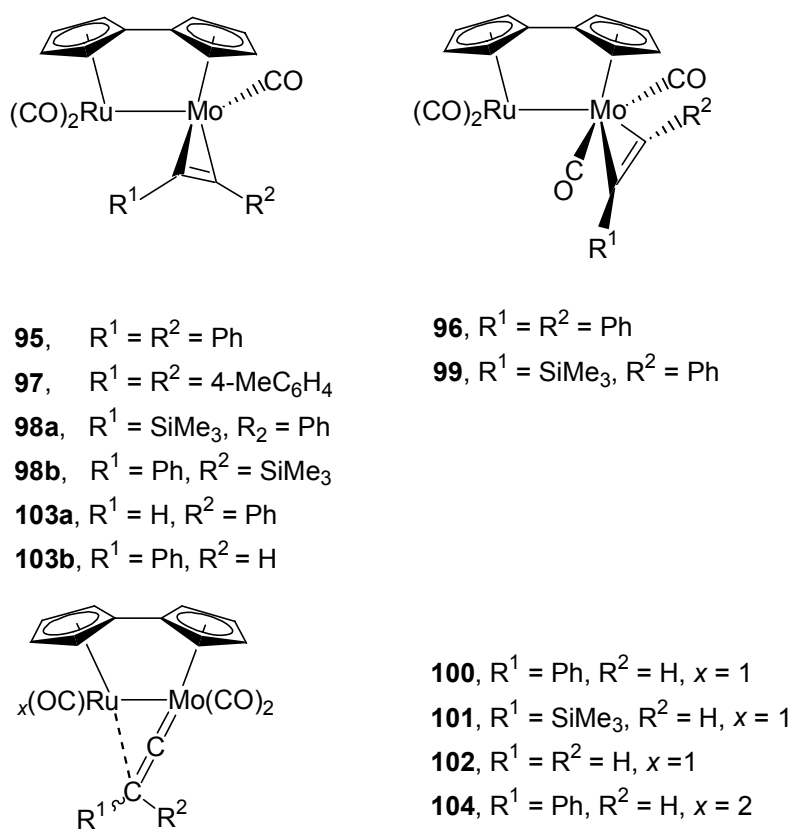
2.2.2. Reactivity

With reasonably efficient preparations of heterodinuclear complexes in hand, some forays have been made into the investigation of their chemistry, all of which have been quite rewarding. Some selected examples follow next.

### *The unique reactivity of FvMoRu(CO)₅ with alkynes*

In light of the remarkable photobehavior of **3** (Scheme 15), we decided to look into the ruthenium based system $FvMoRu(CO)_5$, **7**.[14b] While this compound did not (visibly) enter into the photoisomerization manifold traversed by **3**, in the presence of alkynes it underwent selective photo substitution at the Mo center only (Scheme 21).[51] Thus, irradiation in the presence of diphenylethyne gave **95** and traces of **96**, the latter presumably being a precursor to the former, as **95** readily carbonylated to **96**. The analogous **97-99** were prepared in the same way, whereas **103a**, **b** were derived by protodesilylation of **98a**, **b** at -78 ºC. The rotamers **a** and **b** underwent thermal equilibration on the NMR time scale and could not be isolated separately. The unusual end-on, parallel (and symmetrical) configuration of the two-electron donating alkynes in **96** and **99** contrasts the perpendicular arrangement in the four-electron donating alkyne complexes of the type **95** (Scheme 21). In addition to alkyne rotation, **95** and **97** exhibited a fluxional process that equilibrates the two halves of the respective Cp ligands (^{1}H NMR), presumably via a species containing doubly bridging carbonyls and a symmetrically positioned terminal alkyne ligand.

The role of the ruthenium was changed from that of a spectator to that of an active participant in the case of terminal alkynes **103** which (already at -40 ºC!) were subject to alkyne-alkenylidene isomerization to **100** with remarkable facility.[52-54] Indeed **100** and **101** could be prepared directly from **7** and the respective terminal alkynes. They exist as equilibrating mixtures of isomers, established by an NMR study of the parent vinylidene **102** to be due to vinylidene rotation, possibly proceeding through a non- or semibridging isomer. The first demonstration of the existence of the latter was provided by an X-ray structural analysis of **104**, obtained by (reversible) carbonylation of **100**. To date there seems to be only one other example of such a species,[54a] much better known for other bridging ligands, such as CO and CS. All of this chemistry is very different from that of the corresponding homodinuclear analogs **3** and **5** (Schemes 15 and 8, respectively), a remarkable demonstration of heterodinuclear diversity.

**95**, $R^1 = R^2 = Ph$

97, $R^1 = R^2 = 4\text{-MeC}_6\text{H}_4$

98a, $R^1 = SiMe_3$, $R_2 = Ph$

98b, $R^1 = Ph$, $R^2 = SiMe_3$

103a, $R^1 = H$, $R^2 = Ph$

103b, $R^1 = Ph$, $R^2 = H$

96, $R^1 = R^2 = Ph$

99, $R^1 = SiMe_3$, $R^2 = Ph$

100, $R^1 = Ph$, $R^2 = H$, $x = 1$

101, $R^1 = SiMe_3$, $R^2 = H$, $x = 1$

102, $R^1 = R^2 = H$, $x = 1$

104, $R^1 = Ph$, $R^2 = H$, $x = 2$

Scheme 21

In this vein, the oxidation of **95** with O_2 gave the molybdenum-oxo species **105**, which could then be converted back to $FvMoRu(CO)_5$ **7** under moderate pressures of carbon monoxide.[29,51] The sequence shown in Scheme 22 can be viewed as a stepwise model for the catalytic oxidation of CO by O_2 to give CO_2, and it seems to strengthen the notion that synergistic effects can be observed in heterobimetallic fulvalene compounds. Interestingly, **105** also polymerizes alkynes catalytically,[29] a process that is now under renewed scrutiny.

7 → **95**

hν, Ph—≡—Ph

−CO$_2$, CO, −Ph—≡—Ph

O$_2$ / −CO$_2$

105
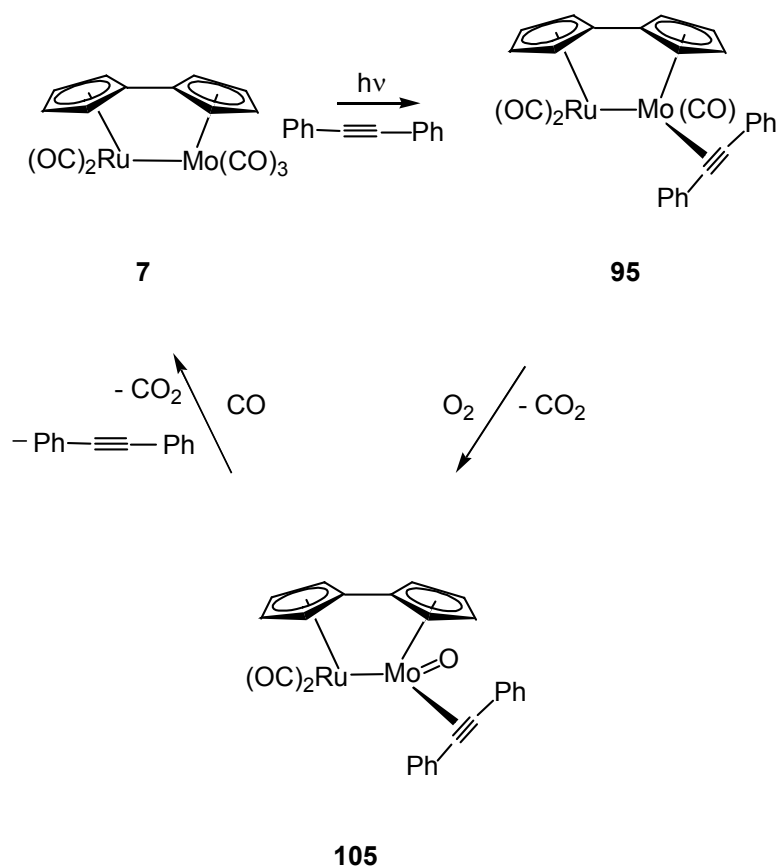
Scheme 22

Photo- and thermal reactivity of Fv[W(CO)$_3$Me][Rh(CO)$_2$]

A second example constitutes the photochemistry of Fv[W(CO)$_3$Me][Rh(CO)$_2$] **82**[47b] and its molybdenum analog, chosen in part as a model system on which to probe potential alkyl group migrations, because of the possibility of W-Me C-H activation by the neighboring CpRh(CO)$_2$, and finally for the pragmatic reason that the relevant behavior of the respective CpM units in **82** had been well investigated.[56] In the event,[55] **82** underwent photodercarbonylation to the M-M bonded **106**, which further rearranged by methyl migration to **107** (Scheme 23).
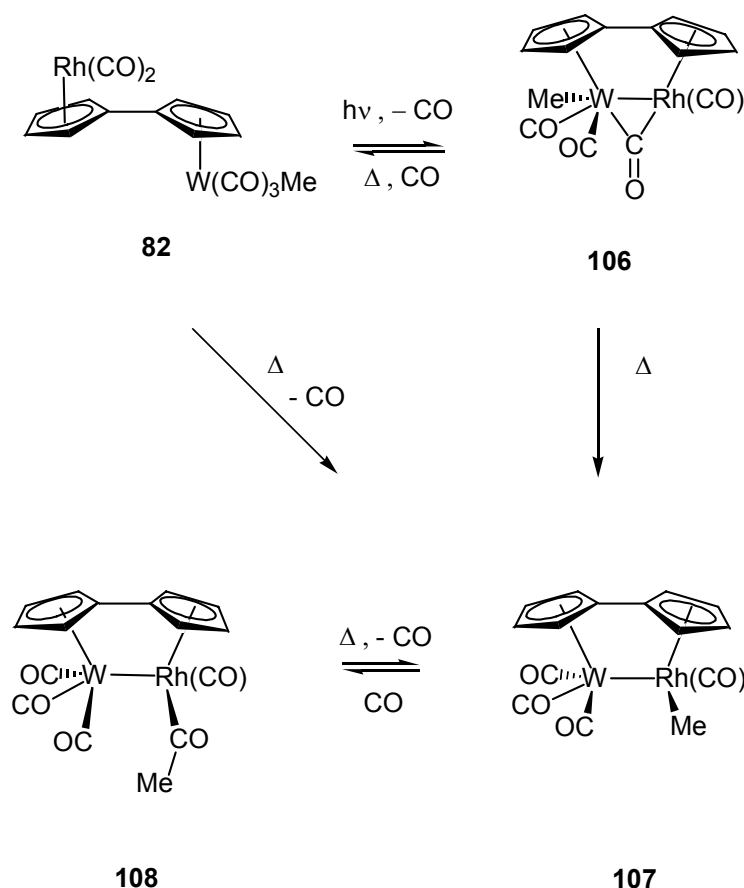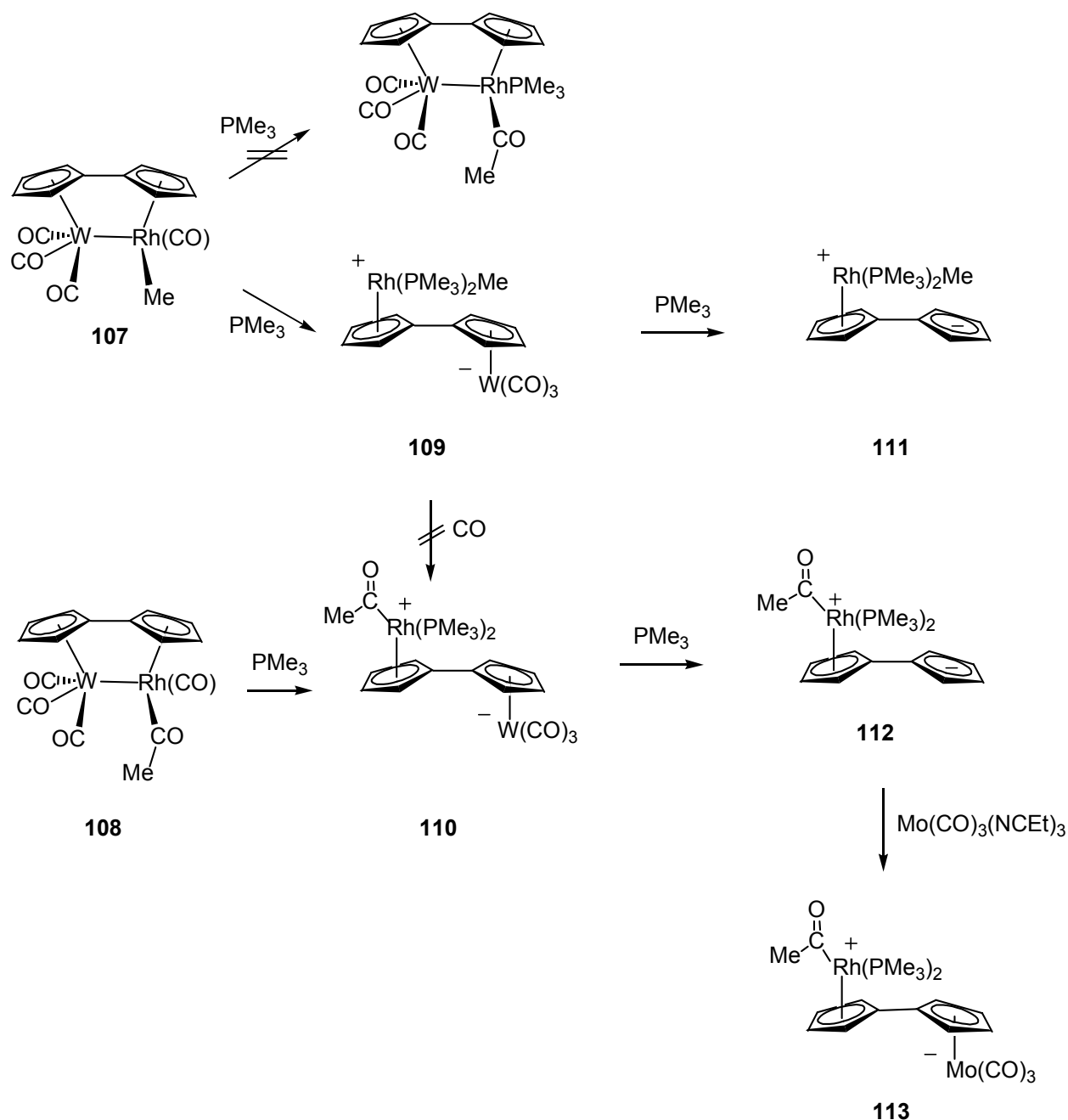
Scheme 23

The same final product could be obtained directly from **82** on heating to 110 ºC. That the thermal process was mechanistically distinct from the photochemical variant was indicated by the ready, reversible carbonylation of **107** to **108**, suggesting the latter as an intermediate in the absence of light. This notion was supported by the chemistry of the (presumed) Mo analog of **82**, which, on attempted synthesis from **80** (Schemes 19 and 20), spontaneously rearranged at ambient temperatures to the Mo version of **108** (similarly subject to thermal decarbonylation to the framework present in **107**). The heterodinuclear complex **108** exhibits an unusually long W-Rh bond of 2.990 (1) Å.

The mechanisms of these processes could be elucidated in greater detail using matrix isolation photochemical techniques and ^{13}C labeling experiments. The key conclusions are that: 1. Complex **82** is selectively photodecarbonylated at the W center to presumably furnish **106** by (possibly direct) addition to the Rh=C=O bond; 2. Complex **107** thermally transforms to **108** by likely regioisomeric retrocycloaddition to Fv[W(CO)₃Me]Rh(CO) which continues by insertion into the W-Me bond; 3. the thermal generation of **107** from **82** involves decarbonylation at Rh (in stark contrast to 1.) through the intermediacy of **108**; 4. a plausible mechanistic scheme connecting **82** with **108** has as its key feature the well known equilibration of the CpW(CO)₃Me unit with its CpW(CO)₂COCH₃ isomer, providing the necessary coordinative unsaturation to allow M-M bond formation and eventual acetyl transfer.

In an attempt to effect CO insertion in **107** in the presence of an external ligand other than CO (which results in **108**; Scheme 23), the complex was treated with PMe$_3$. Interestingly, the (now familiar) zwitterion chemistry depicted in Scheme 24 occurred, providing first **109**, then **111**. Similarly, **108** gave **110** and **112**. The latter was reacted with Mo(CO)$_3$(NCEt)$_3$ to give zwitterionic **113**.
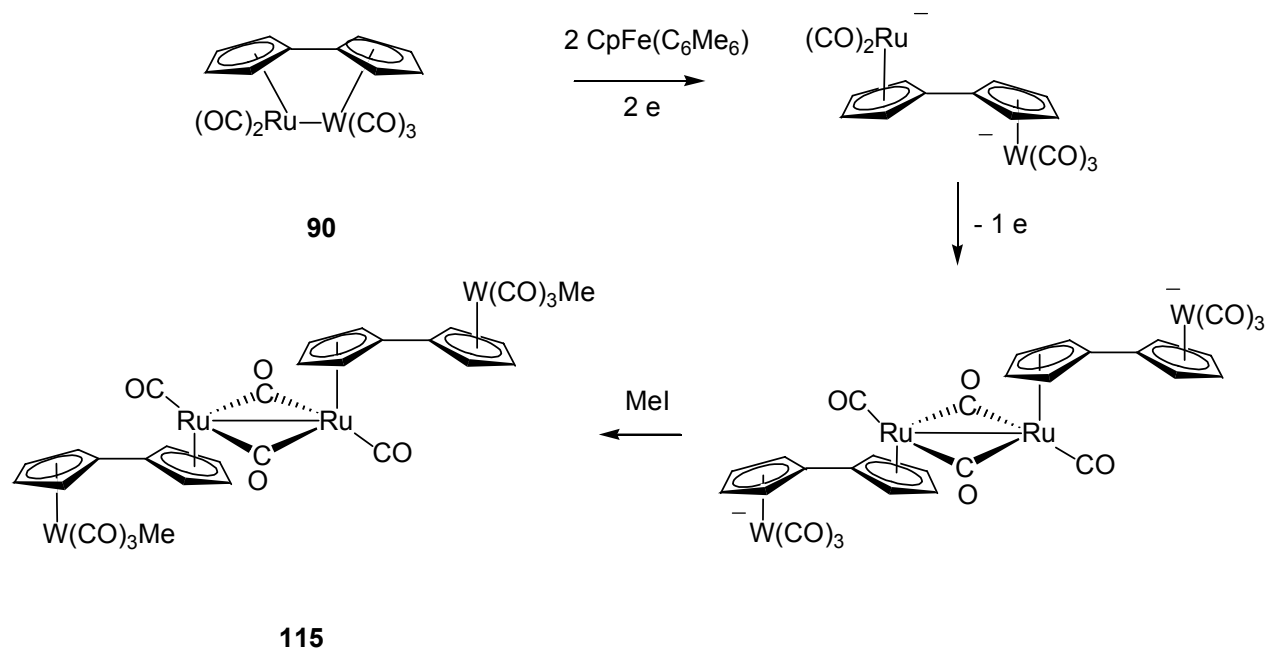

Scheme 24

Redox chemistry

A third project in which heterodinuclear Fv complexes played an important role was executed in collaboration with the group of Astruc at Bordeaux,[4a] significantly expanding on earlier work with Bard in Austin.[57] The latter established the electrochemistry of **3-7** as reflecting the relative ease of reductive cleavage of the M-M bond by 2e processes and probed the mechanism of reoxidation of the dianions. With Astruc (and Delville), we became interested in whether the communication through the Fv bridge would allow for specific metal "recognition" in heterodinuclear systems. Thus, the electrochemistry of heterobimetallic complexes FvWFe(CO)$_5$ **89** and FvWRu(CO)$_5$ **90** was investigated. The former was reduced in two successive one-electron steps (slow-fast), and this behavior was synthetically exploited by using the one-electron transfer agent CpFe(C$_6$Me$_6$) to prepare the tetranuclear dimer **114** by selective metal reduction, dimerization, and trapping by methyl iodide (Scheme 25).
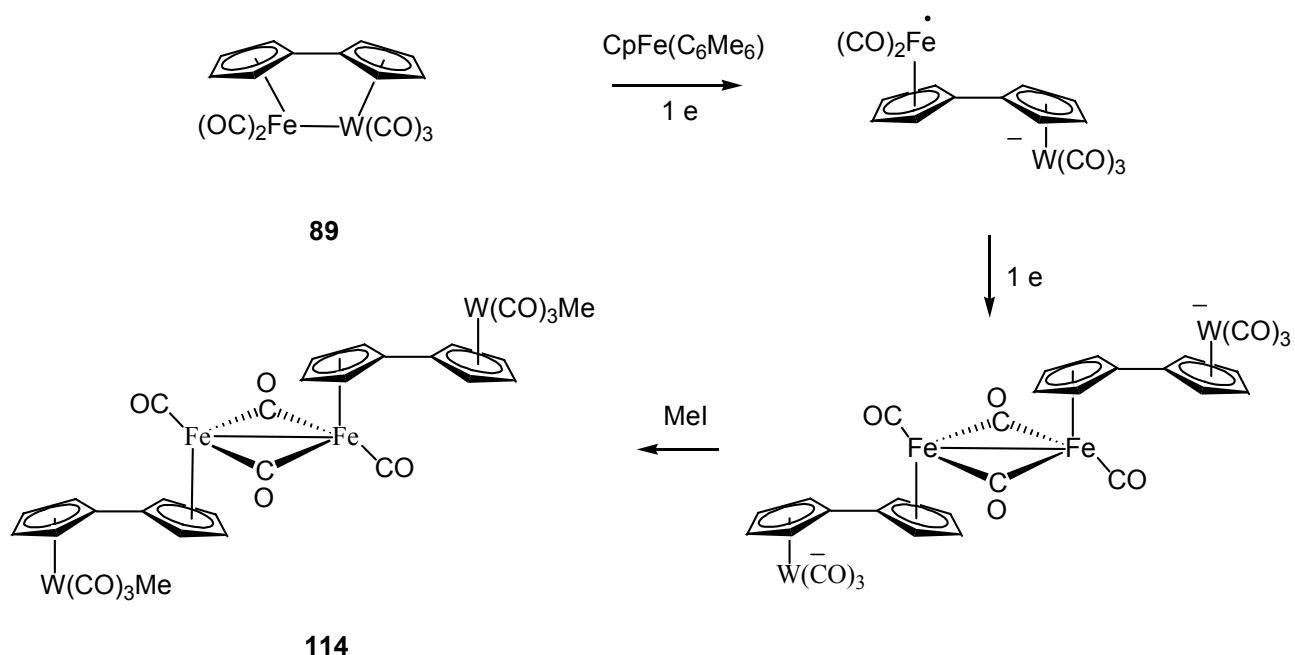
Scheme 25

In contrast, complex **90** reduced slowly in a two-electron step [or, preparatively, using CpFe(C$_6$Me$_6$)] to the dianion. Upon reoxidation (anode or with Cp$_2$Fe$^+$PF$_6^-$), selective metal coupling occurred to eventually allow the isolation of **115** (Scheme 26).

Scheme 26

This redox behavior led to an investigation of the use of electrocatalysis to effect metal-specific ligand substitution.[59] It was found that reduction of **89** with a catalytic amount of $CpFe(C_6Me_6)$ in the presence of excess $P(OMe)_3$ or PMe_3 led to the formation of the zwitterions $Fv[W(CO)_3^-][Fe(CO)PR_3^+]$ (R = Me, OMe).

Interestingly, **90** displayed unique behavior with different reducing agents, as the monosubstituted zwitterion $Fv[W(CO)_3^-][Ru(CO)_2(PMe_3)^+]$ was obtained when $CpFe(C_6Me_6)$ was used, while the disubstituted complex $Fv[W(CO)_3^-][Ru(CO)(PMe_3)_2^+]$ was formed when $Cp*Fe(C_6Me_6)$ was the catalyst. This electrocatalytic process was generalized to include the homobimetallic species $FvMo_2(CO)_6$ (**5**) and $FvW_2(CO)_6$ (**6**), allowing the preparation of previously reported zwitterions $Fv[M(CO)_3^-][M(CO)_2PMe_3^+]$ (M = Mo, W) under milder conditions, completely obviating the occurrence of ring slippage (Section 2.1.2.). Zwitterions of this type may have applications in nonlinear optics.[60]

2.2.3. Conclusions

The heterodinuclear fulvalene complexes described above differ in photo- and thermal reactivity from comparable homonuclear analogs. Thus, under the same conditions, **7** reacted quite differently from its homodinuclear analogs **3** and **5** in the presence of alkynes. Moreover, none of the fulvalene dimetals investigated so far have effected C-C bond formations with alkynes, such as those typically observed with CpM dimers. It is curious why this should be so, and further experimentation is in order.

With respect to the chemistry of **82** (and its Mo analog), distinct metal-specific decarbonylation pathways were uncovered, in addition to a unique methyl migration process from W to Rh.

Fundamentally, such ligand migrations along a metal chain are important prerequisites for the attainment of synergistic (or at least cooperative) catalysis.[61]

Finally, specific metal selectivity was observed in the reactions of **107** and **108** with phosphines and in the reductive couplings of **89** and **90** to give **114** and **115**, respectively. In both cases kinetic and thermodynamic factors may play a role, details that need to be worked out in the future.

3.   Tercyclopentadienyl Metal Complexes

3.1. Synthesis and structural characterization

Armed with the considerable knowledge of FvM_2 complexes exemplified in the previous sections, about a decade ago we embarked on expanding the Fv motif to incorporate cyclopentadienologs, i.e. cyclopentadienyl substituted Fv systems, the first member of the series being tercyclopentadienyl (terCp). The "unnatural" topology of three metals held in close proximity by the tightly bound π ligand seemed to promise rich chemistry.[62]

On the basis of the transformations described in Schemes 19 and 20, two routes to these systems were developed. The first starts with fulvalene dianion and exploits the deactivating nature of the first vinyligous alkanoylation with 3-chlorocyclopentenane on the resulting fulvalene frame to achieve selective monosubstitution (Scheme 27). Deprotonation in situ provided the two regioisomeric 3-oxocyclopentenylated fulvalene dianions which were worked up in two ways: either metallation followed by oxidative M-M bond formation to give **116** and **117**, or metallation followed by methylation to furnish **118**. Chromatography at this stage separated components **a** from **b**. The appended cyclopentenone was then elaborated as described in Schemes 19 and 20 to result in **121 - 128**.
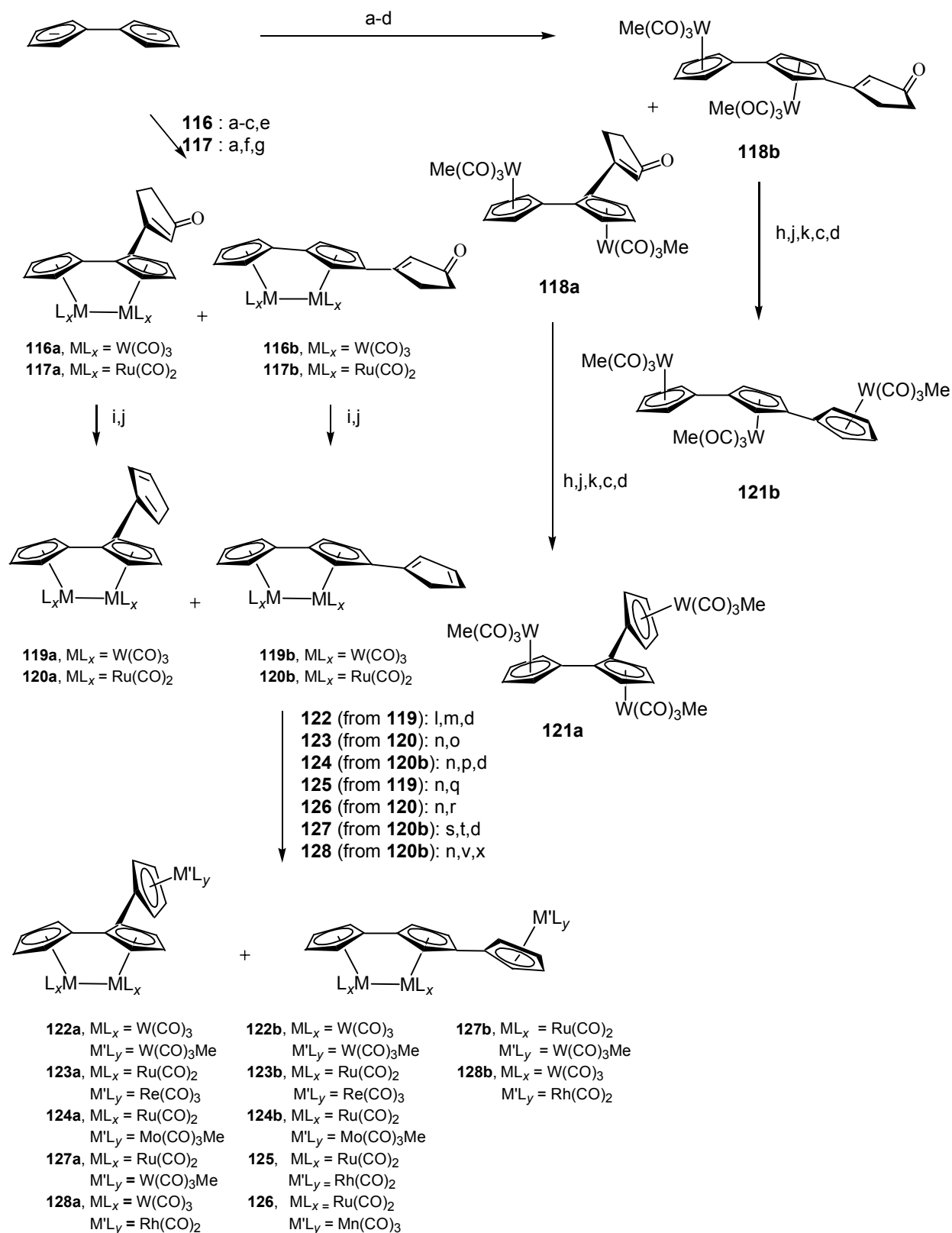
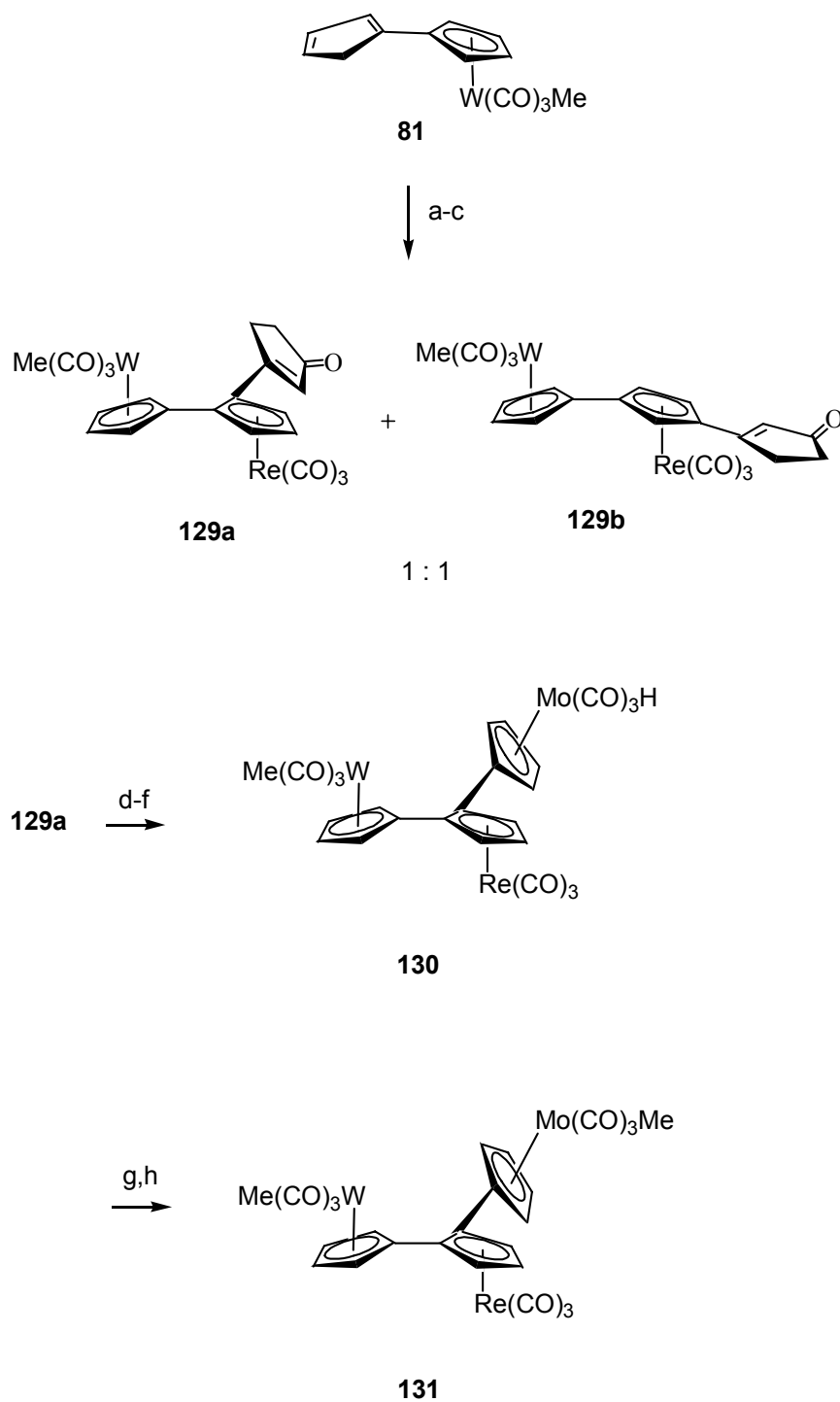**Scheme 27** a) 3-Chloro-2-cyclopentenone, THF, -78°C, 5 min; b) BuLi, -78 °C to 23 °C; c) [W(NCEt)$_3$(CO)$_3$] excess, DME, 23 °C, 3 h; d) MeI, 23 °C, 30 min; e) AgBF$_4$ (2.2 equiv.), THF,

-78 ^{o}C to 23 ^{o}C, 12 h; f) MeCO$_2$H, -78 ^{o}C; g) [Ru$_3$(CO)$_{12}$], DME, 18 h; h) LiAlH$_4$, Et$_2$O, 0 ^{o}C to 23, 1h; i) iBu$_2$AlH, CH$_2$Cl$_2$, 0 ^{o}C, 2 h; j) cat. 4-MeC$_6$H$_4$SO$_3$H, C$_6$H$_6$, 60 ^{o}C, 2 min; k) KOtBu, DME, 23 ^{o}C, 10 min; l) [W(CO)$_3$(NCEt)$_3$], THF, 23 ^{o}C, 12 h; m) LiN(SiMe$_3$)$_2$, THF, -78 ^{o}C, 5 min; n) NaNH$_2$, THF, 23 ^{o}C, 5 min; o) [Re(CO)$_3$Br(THF)]$_2$, THF, 23 ^{o}C, 1 h; p) [Mo(NCMe)$_3$(CO)$_3$], THF, 23 ^{o}C, 30 min; q) [Rh(CO)$_2$Cl]$_2$, THF, 23 ^{o}C, 1 h; r) [Mn(CO)$_4$Br]$_2$, THF, 23 ^{o}C, 30 min; s) KOtBu, THF, 23 ^{o}C, 5 min; t) [W(NCMe)$_3$(CO)$_3$], THF, 23 ^{o}C, 30 min; u) KH excess, THF, 5 min; v) DIBAL-H, CH$_2$Cl$_2$, 0 ^{o}C, 2 h; x) [Rh(CO)$_2$Cl]$_2$, THF, 1.5 h.

It is possible to carry out the initial alkenylation of Fv dianion with selectivity for either series **a** (α-attack) or **b** (β-attack). Thus, using dilithiofulvalene at -78 ^{o}C in suspension in THF in step a) of Scheme 27 furnished almost exclusively only **116a**, suggesting kinetic preference for α-attack, even though more sterically encumbered. Such selectivity would be consistent with frontier orbital control in this process.[63] On the other hand, employment of the much less reactive 3-ethoxy- rather than 3-chlorocyclopentenone as the reagent, led to exclusive formation of **116b**.[64]

The second strategy stitches the Cp rings together one at a time and is therefore advantageous in the metal sequence specific assembly of heterotrimetallic arrays. Thus, for example, **81** (made as described in Section 2.2.1. according to Scheme 19 or by Pd coupling methodology) can be further elaborated via the reaction of its anion with 3-chlorocyclopentenone (Scheme 28) to **129a**, **b**. Both regioisomers can then be subjected to a final metallation sequence,[62,64] as shown for **129a** in Scheme 28, providing **130** and **131**.[62]

Scheme 28 a) NaH (3 equiv), THF, 0 °C, 20 min; b) 3-chloro-2-cyclopentenone, 0 °C, 1.5 h, then 23 °C, 30 min; c) [Re(CO)₃Br(THF)]₂, THF, 4.5 h; d) iBu₂AlH, CH₂Cl₂, 0 °C, 2 h; e) 4-MeC₆H₄SO₃H, C₆H₆, 60 °C, 2 min; f) [Mo(NCMe)₃(CO)₃], THF, 23 °C, 19 h; g) KOtBu, THF, 23 °C, 40 min; h) MeI, 23 °C, 2.5 h.

Another complementary example illustrates an application in the β-terCp series, containing a Fv(M^1-M^2) fragment, and rests in part on the chemistry described in Scheme 23 (Scheme 29).[64]
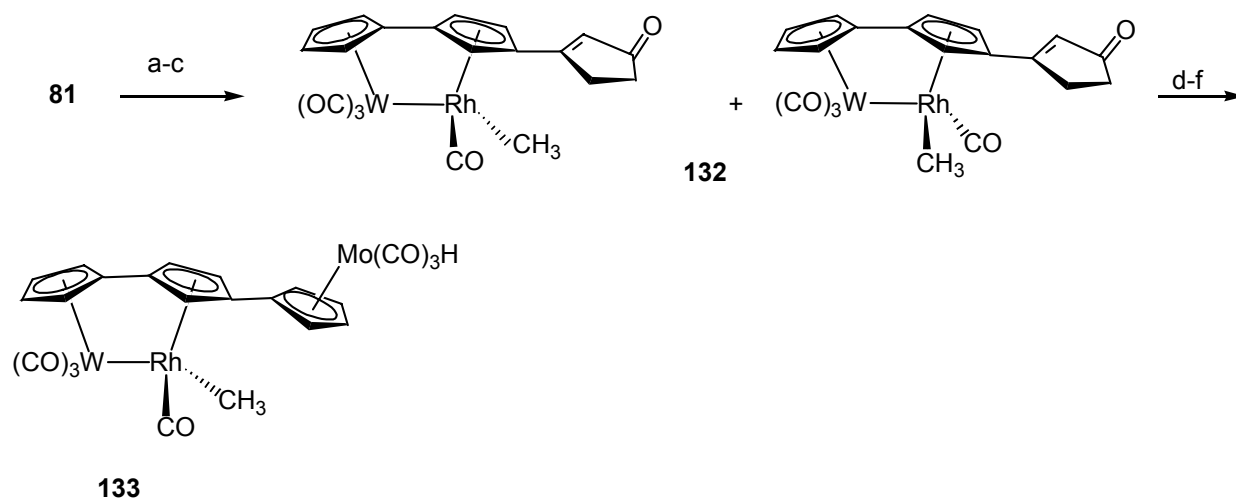
Scheme 29 a) NaH; b) 3-chlorocyclopentenone; c) NaH, THF, [Rh(CO)$_2$Cl]$_2$, -20 °C to reflux, column chromatography; d) iBuAlH; e) 4-MeC$_6$H$_4$SO$_3$H; f) Mo(NCEt)$_3$(CO)$_3$.

Unlike **107**, intermediate **132** can (and does) exist as two diastereomers, shown to interconvert on the NMR time scale, whereas only one isomer of **133** was observed. Structurally, the terCp ligand exists as two isomers that differ only in the connectivity of the Cp rings. As already indicated, the central ring may be substituted in either 1',2' (α isomer) or 1',3' fashion (β isomer). It is apparent from X-ray crystallographic studies that in the α isomer there is a steric interaction that is responsible for a relatively large twist angle between one of the terminal Cp rings and the attached FvM$_2$ fragment. When there is a Fv(M-M) bond (as, e.g., in **123a**[62], the twist angle is larger than 90°, with the attached metal minimizing steric interactions with the FvM$_2$ frame. In the absence of an M-M bond [as, e.g., in terCpMo$_3$(CO)$_3$Cl$_3$][64] one Cp is nearly perpendicular to an almost coplanar Fv unit with the metals in the anti configuration, again, a sterically most accommodating arrangement. In the β isomer, the terCp array is nearly coplanar, although some twisting and bending is visible, as already noted for simple FvM$_2$ systems (Section 2.1.1.).
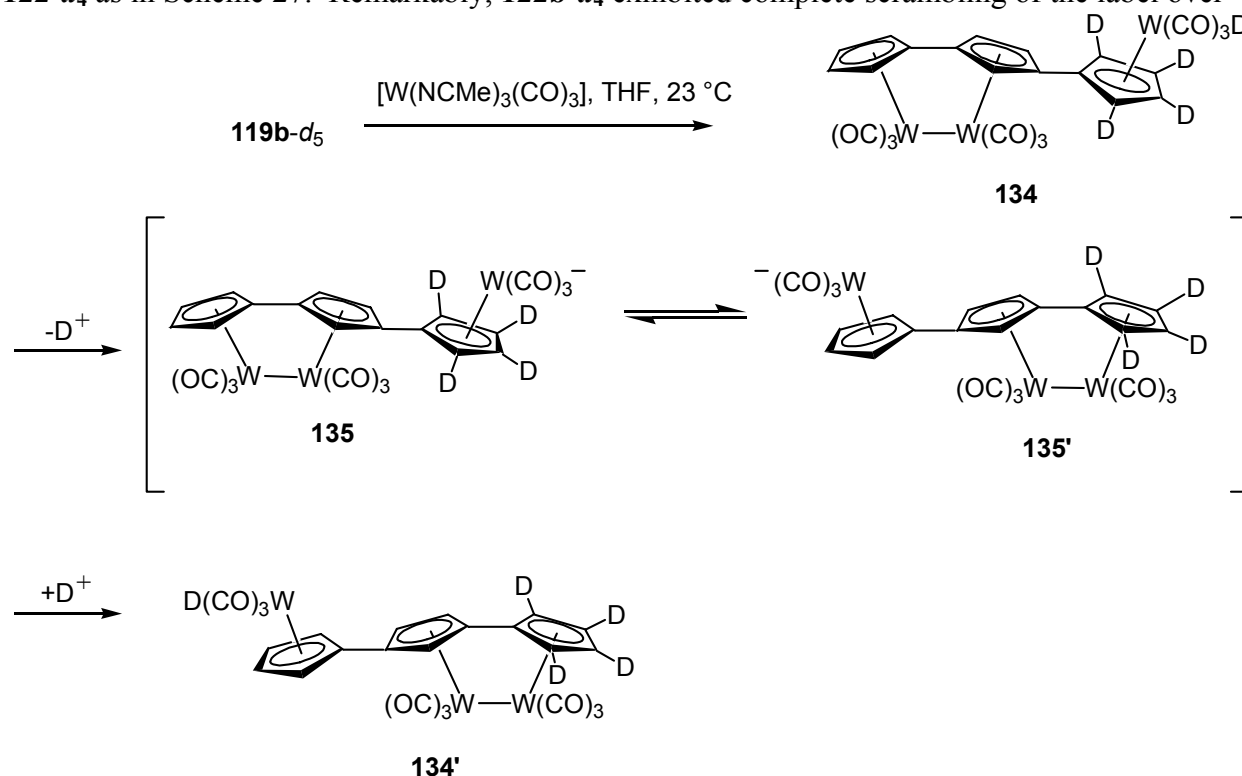
The synthesis of the terCp trimetals allowed their preliminary exploration as potentially cooperating trinuclear constructs.

3.2. Reactivity

3.2.1. Anionic charge transfer

Evidence for charge transfer along the trimetallic chain, a process of fundamental importance,[60] was gleaned from several experiments. Thus, for example, the cyclopentadiene substituent in

119 was readily perdeuterated (D_2O, NEt_3, acetone-d_6) and the resulting species converted to **122-d_4** as in Scheme 27. Remarkably, **122b-d_4** exhibited complete scrambling of the label over


119b-d_5 $\xrightarrow{\text{[W(NCMe)}_3\text{(CO)}_3\text{], THF, 23 °C}}$

134

$\xrightarrow{\text{-D}^+}$ [**135** $\rightleftharpoons$ **135'**]

$\xrightarrow{\text{+D}^+}$ **134'**

Scheme 30

the two terminal Cp rings, whereas **122a-d_4** showed retention.[62] Following the course of the reaction of **119b-d_5** with [W(NCMe)$_3$(CO)$_3$] by ^{1}H NMR indicated that the initial metal deuteride **134** was generated label-specifically, but that it underwent equilibration with regioisomer **134'**, (Scheme 30). This process was accelerated by base, retarded by acid. A plausible mechanism for the label scrambling is the reversible formation of the anion **135**, rapidly isomerizing to **135'** (Scheme 30), as the pK_a of **134** would be expected to be comparable to that of **45** (Section 2.1.2.)[24a] and CpW(CO)$_3$H (~ 16).[65] The degenerate isomerization of **135** is unique in its simplicity and constitutes an intramolecular variant of the known and mechanistically complex nucleophilic attack by anionic metal centers on dinuclear complexes.[66] As such it provides an opportunity to study this process was under potentially less complicated circumstances, currently in progress, thus perhaps pinpointing one of the three most reasonable pathways for exchange:[60] electron transfer via nucleophilic attack directly at the metal with concomitant ring slippage of the central Cp or CO dissociation; direct nucleophilic attack at a central CO ligand; and one-electron transfer, followed by decay of the radical anion, and finally combination of the resulting 17 electron radicals.

Why should the rate of such an equilibration be less in the α-isomer of **135**? It appears that steric encumbrance to (normally fast)[67] rotation of the CpM$^-$ unit is to blame, thus preventing the perhaps required (near) coplanarization of the terCp ligand and therefore sufficient proximity of the active centers.

3.2.2. Radical electron transfer

A topologically very similar result to that described for **135**, but presumably involving its radical counterpart, was obtained on treatment of regiopure **134** (or its α-isomer) with CCl_4: complete scrambling (or retention) of label was evident in the resulting chloride **136** (Scheme 31).[62]
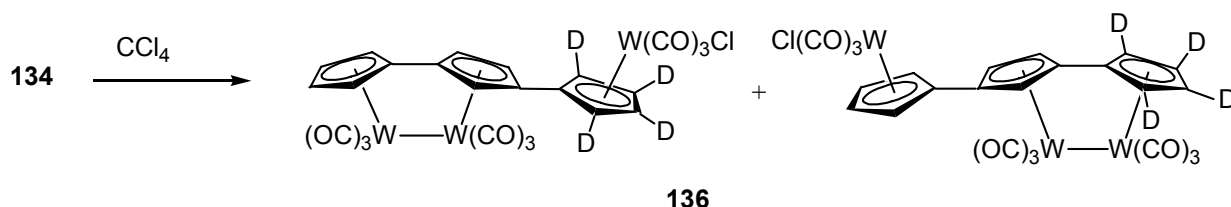
Scheme 31

3.2.3. Methyl transfer

One of the prerequisits for potentially synergistic catalysis by terCp trimetals is that intramolecular ligand transfer is facile. In this way, one can envisage metal specific activation of two organic substrates (especially in designed heterotrinuclear systems) and subsequent transformation of the resulting organic fragments. To probe the feasibility of such a process, complex **122b** was scrutinized. However, the appropriately regiospecifically labeled **122b-d_4** was stable towards rearrangement, even on irradiation.

On the other hand, reduction of the W-W bond provided a dianion,[137] for which methyl migration to **138** was clearly visible by ^1H NMR spectroscopy and trapping with CD_3I (Scheme 32). The
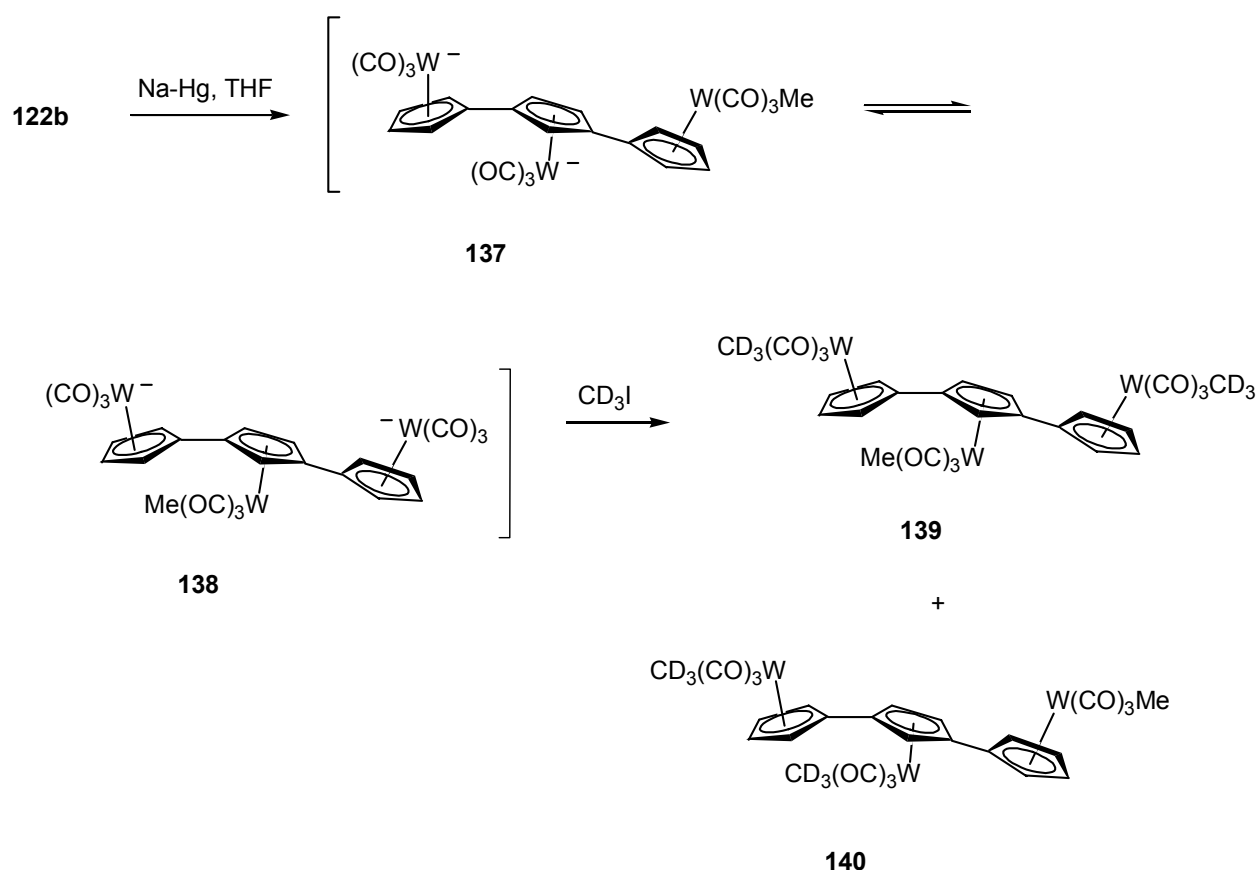
Scheme 32

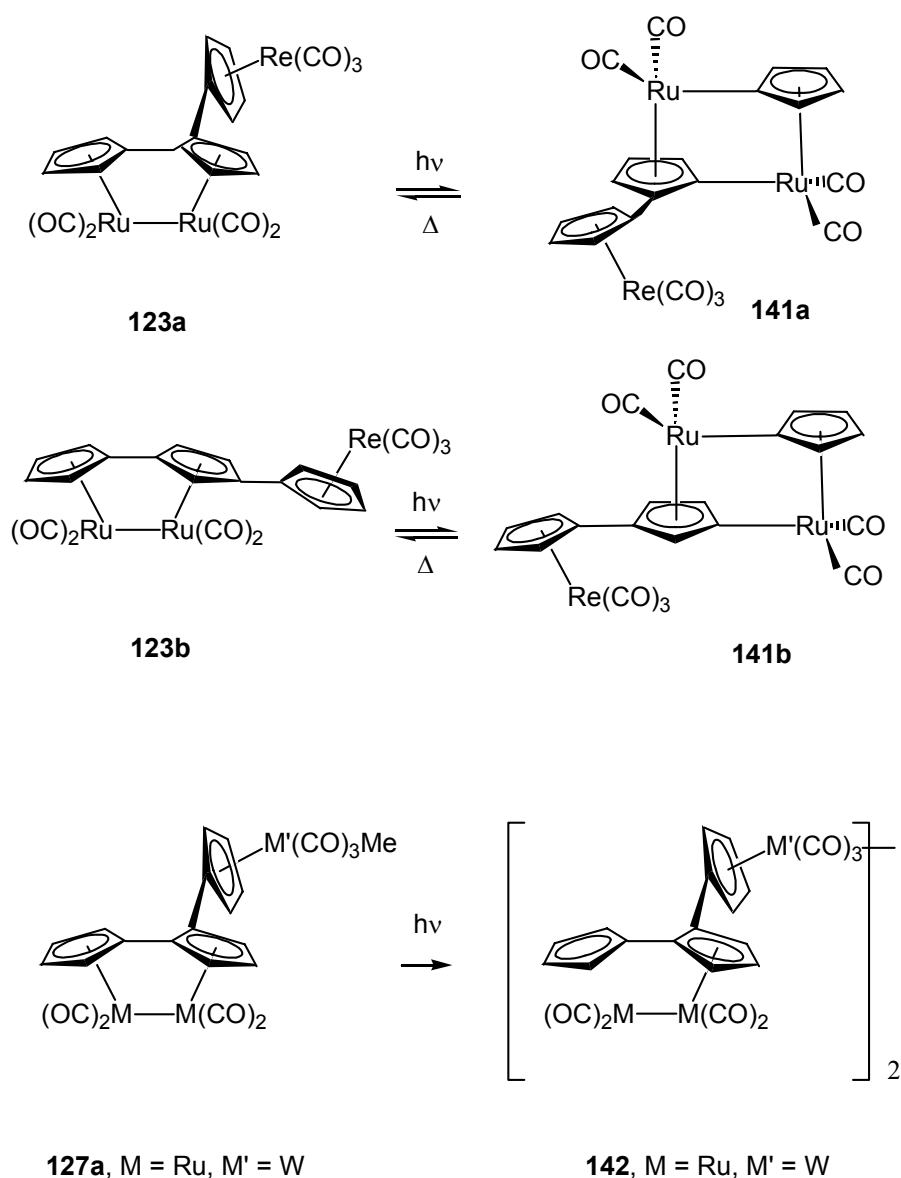equilibrium mixture of the dianion contained **138**: **137** in a ratio of 2.7:1 initially, changing to 6:1. The thermodynamic dominance of **138** in this equilibrium might be expected on the basis of charge separation. The two isomeric dianions alkylate at comparable rates, as the methyl derivatives **139** and **140** were generated in a 2.4:1 ratio. Most significantly, a crossover experiment employing **122b** and its $[(\eta^5\text{-}C_5D_4)W(CO)_3(CD_3)]$-substituted counterpart provided the final trimethylated products without any evidence for intermolecular label scrambling. In addition, an identical series of experiments starting with the α-isomer **122a** gave analogous results. It thus appears that in the latter, rescinding the conformational rigidity inherent in the Fv(M-M) part of the framework provides enough flexibility for the observed methyl transfers.

There is precedence for the intermolecular methyl (and alkyl) transfer from alkylmetals to metal ion complexes, and mechanistic studies reveal a more complex picture than might be envisaged on the basis of the analogy to the organic S_N2 process.[68] Again, further mechanistic scrutiny of the terCp system in this regard might prove fruitful because of its strictly intramolecular constraints and ease of analysis.

3.2.4. Some tantalizing photochemical experiments

Preliminary experiments provide a glimpse of potentially rewarding photochemistry of the terCp trimetallic array.[64] These experiments were carried out on systems for which the reactivity of the individual subunits under similar conditions had been well established (vide supra). Examples

are shown in Scheme 33, in which the potential effect of the FvRu$_2$(CO)$_4$ core on the dynamics of the appended CpM unit was probed. Thus, irradiation of **123a** or **b** reproduced the analogous

123a $\xrightleftharpoons[\Delta]{h\nu}$ **141a**

123b $\xrightleftharpoons[\Delta]{h\nu}$ **141b**

127a, M = Ru, M' = W $\xrightarrow{h\nu}$ **142**, M = Ru, M' = W

Scheme 33

isomerization of **3** (Schemes 15-17) faithfully. The resulting **141a** and **b** underwent clean thermal reversal with activation parameters very similar to those of **55** (Scheme 17). Therefore, the excited state of this system appears to chemically transform according to the component chromophore of **3**. In contrast, the W analog **127a** shows the chemistry typical of the CpW(CO)$_3$Me substituent to give **142**, whereas its β isomer **127b** decomposes. Similar results to those with **127** were obtained with **122a** and **b**. The electronic spectra of the terCp complexes seem to be a composite of those of the individual chromophores, but the absorptions are bathochromically shifted, more so for the β than the α isomers, perhaps a reflection of the

difference in effective π overlap along the chain. For **122** and **127**, the electronic absorptions of the substructures overlap conderably,[35a,40] and the selective photoreactivity at the CpW(CO)$_3$Me end is interesting. Such also occurred in the presence of alkynes (Scheme 34), resulting in the typical[35d,69] insertion products **143** - **146**, even in the presence of excess added ligand, remarkable, in light of the multitude of imaginable products.

122a

143, R = Et, R' = Ph
144, R = R' = Me
145, R = H, R' = Ph

127b

146
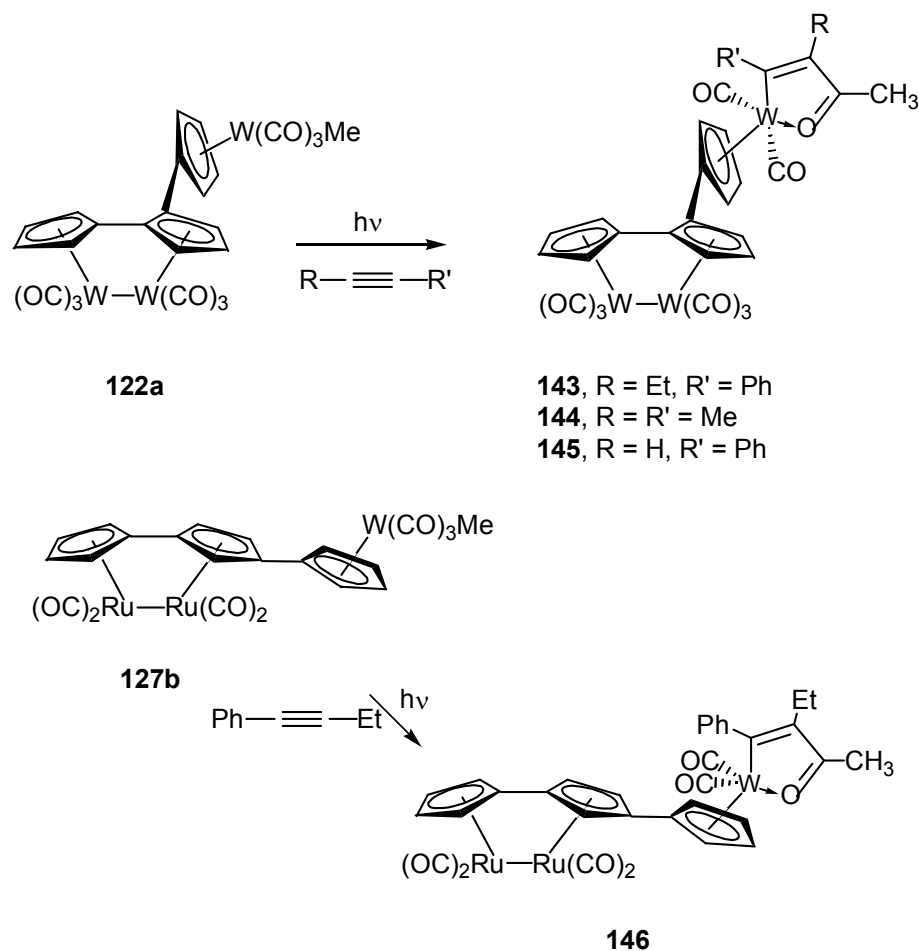
Scheme 34

3.2.5. Conclusions

It is clear that our methodology provides ready access to terCp trimetals with extensive, if not complete, control of metal, loco-, and ligand regioselectivity. The chemistry of the plethora of complexes now available is only in its infancy, but the preliminary data do show extensive intrachain communication, the possibility of intramolecular ligand migration, and the possibility of selective transformations in good yields, despite the multifunctional nature of the substrates. We hope to exploit these findings in the specific construction of trimetallic sequences whose identity may be conducive to synergistic catalysis.
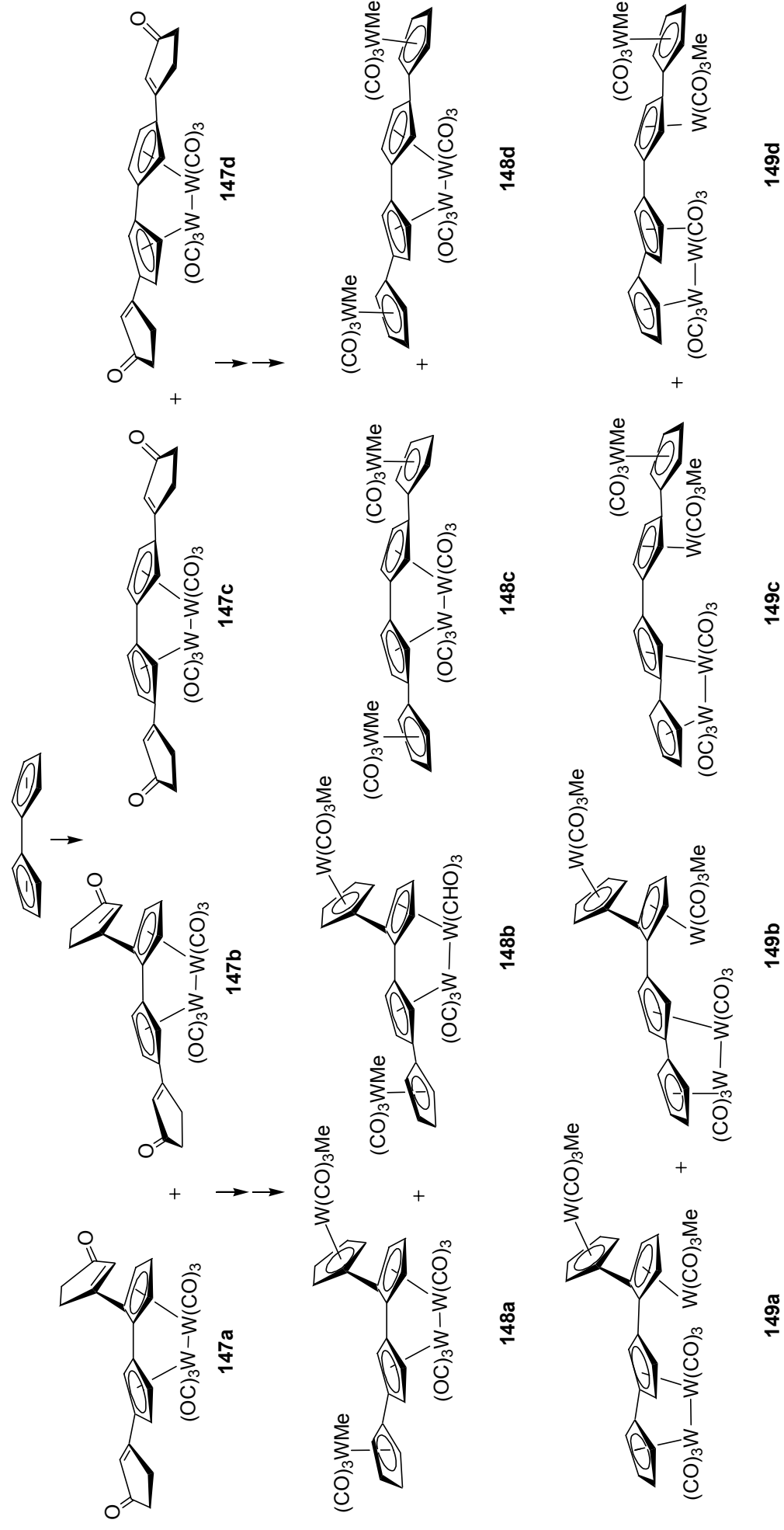
4. Quatercyclopentadienyl Metal Complexes

The strategies employed in the assembly of the terCp ligand (Schemes 27 and 28) are, in principle, readily adaptable to its higher cyclopentadienologs. However, there are two facets of these approaches that render them it increasingly difficult to realize. One has the drawback that is inherent to any interactive sequence to oligomers: if the yield of each step is not close to quantitative, the efficiency of the scheme rapidly decreases to the point of impracticability. The second is built into the topology of the disubstituted internal CpM unit of the growing chain: it is stereogenic and may give rise to stereoisomers, in addition to the possibility of α and β structural isomers already encountered in terCpM$_3$. For the next higher oligomer, homonuclear quaterCpM$_4$, this translates into the possibility of six isomers. This number rapidly increases if one considers M-M bonded isomers and heteronuclear analogs. Thus, one can readily envisage formidable synthetic obstacles.

In the event (and to quantify the above), Scheme 35 was executed,[70] in a manner completely analogous to that for **122** in Scheme 27, but adjusting for the changed stoichiometry of the oxocyclopentenylation step. The results reveal that the initial double cyclopentenylation sequence to give isomers **147** avoids the generation of the two α,α'- regioisomers.

While this selectivity limits the number of isomers of **147** to four, continued execution of the Scheme doubles it, because of the possibility of M-M bond isomers, as in **148** and **149**. (Partial) separation of isomers along the sequence was possible at various stages by column or preparative thin layer chromatography and by fractional crystallization. The structural assignments were made on the basis of X-ray analysis (**147a** and **b**) and extensive ^{1}H NMR experiments. The final products **148** and **149** were isolated in milligram quantities, representing low overall yields from fulvalene dianion. However, while these results seem forbidding, it should be possible to improve on them by increasing the regioselectivity of the first step (see Section 3.1.) and by avoiding the possibility of M-M bond isomerism through a judicious choice of the conditions for the final step in Scheme 35.

Because of the only minute quantities available of the quaterCpW$_4$ isomers **148** and **149**, no chemistry could be executed on these complexes. Such would be interesting, as it is clear that their precursor dianions are equilibrating by a combination of the electron transfer and ligand migration steps described in Sections 3.2.1. - 3.2.3. for the terCpM$_3$ system.
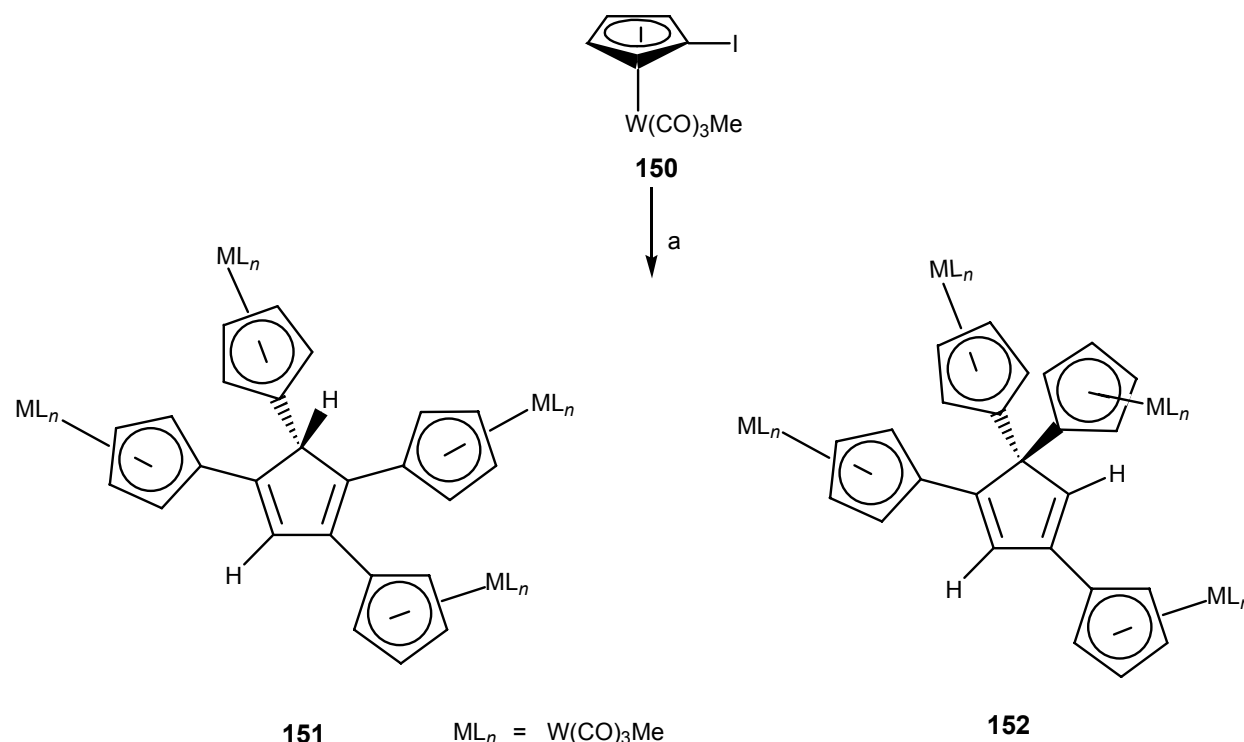
Scheme 35

5. Penta(cyclopentadienyl)-η^5-cyclopentadienyl Metal Complexes

5.1. Synthesis and structural characterization

A rather dramatic observation was made during the application of the Pd catalyzed


Scheme 36 a) CpSnMe$_3$ (0.3 equiv), 3% [Pd(OAc)$_2$], NaOAc (15 equiv), PhCH$_2$Et$_3$N$^+$Cl$^-$ (5 equiv.), DMF, 23 °C, 52 h.

cyclopentadienylation of the iodide **150** to give **81** (Section 2.2.1.). Thus, using **150** in excess resulted directly in the tetracyclopentadienylated diene substrates **151** and **152** (Scheme 36)![47c]

Even better, this oligocyclopentadienylation could be carried out on cyclopentadiene itself, avoiding the unattractive (and cumbersome) use of the stannylated version. Similar results were obtained for ML$_n$ = Mn(CO)$_3$ and Fe(CO)$_2$Me.[47c] The facile generation of **151** immediately presented as a seemingly reachable target pentacyclopentadienyl(cyclopentadienyl) [pentaCp(Cp)] complexes. This "star" like oligoCp topology is intrinsically theoretically interesting, has the potential of anchoring six metals (if clustered) in a completely novel constellation of a hexanuclear "minisurface" or (if metallocene like) a "Ferris wheel" array, and contains the topography of the elusive "buckybowl" semibuckminsterfullerene, C$_{30}$H$_{10}$ **156** (see Scheme 38).[71]

Unfortunately, attempts to outfit **151** with a fifth CpML$_n$ substituent failed by this method, very likely for steric reasons. Indeed an X-ray structure of **152** already shows severe congestion around the core five-membered ring. To get around this problem, an inverse strategy was employed which proved successful (Scheme 37). Thus, pentaiodocymanthrene **153** was

persubstituted to **154**, which could then be deprotonated to the highly symmetrical pentaanion **155**. In solution, **154** exists as eight equilibrating double bond isomers (with all possible combinations of 1,3- and 1,4-cyclopentadienyl substituent sequences), one of which (shown in drawing **154**) crystallizes to allow for an X-ray analysis.[72] The substituent cyclopentadiene rings


153   **154**

155
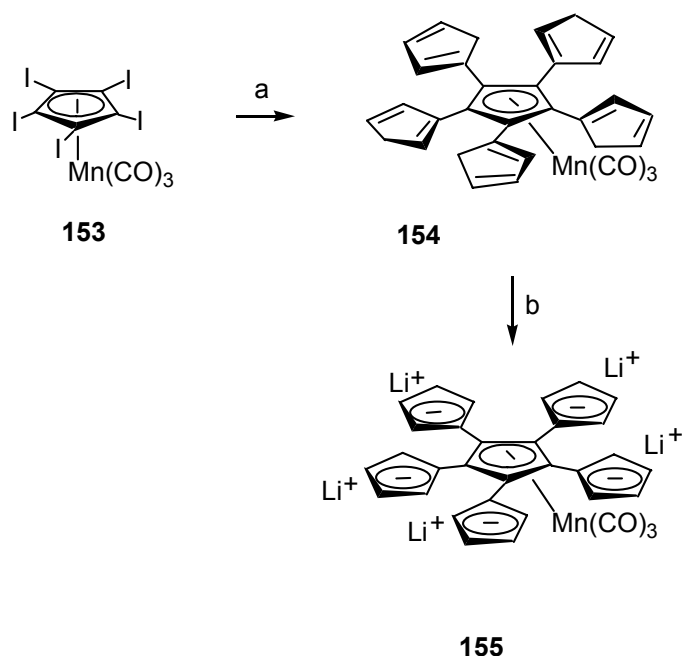
Scheme 37 a) CpSnMe$_3$ (10 equiv), 30% [Pd(CH$_3$CN)$_2$Cl$_2$], DMF, 90 °C, 15 min; b) BuLi (5 equiv), THF, 23 °C, 10 min.

adopt a propeller-like arrangement to minimize steric interactions, with dihedral angles ranging from 42.2 ° to 46.4°.

5.2. Reactivity

Consistent with the crowded environment around the central ring, all attempts at effecting transition metallation of **154** or **155** have failed so far. Instead, electron transfer (in the case of **155**) seems to dominate. However, very interesting coalescence phenomena were observed on laser desorption/ionization (LDI) of **154**.[72] The aim of this experiment was to exploit the connectivity in the starting material to generate **156**, as such (Scheme 38), or as a metal complex. Surprisingly, LDI-mass spectrometry at low laser power revealed initial fragmentation by not only successive loss of CO and eventually the metal, but also loss of one Cp ring. However, no signal for C$_{30}$H$_{10}$ was evident. At higher laser power, fullerenes (mostly C$_{48}$ - C$_{74}$) appeared, with a dominant C$_{50}^{+\cdot}$ ion peak, in addition to a relatively abundant C$_{60}$ signal. An attempt to generate **156** by flash vacuum pyrolysis failed. Perhaps modified analogs of **154** (or **155**) will produce the desired chemistry.
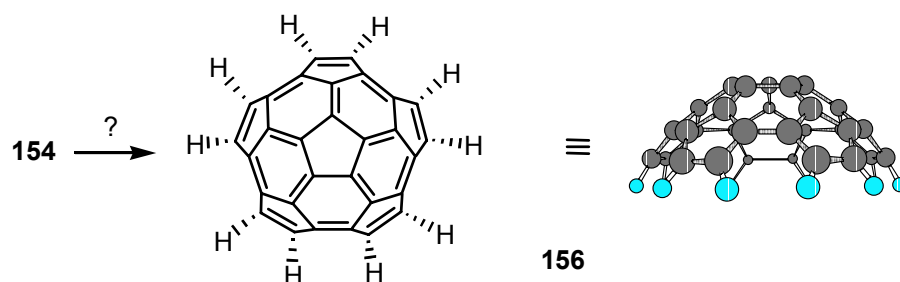
Scheme 38

5.3. Conclusions

While the pentaCp(Cp) framework as present in **154** and **155** has proven to be difficult to harness, its rapid method of production clearly points the way to applications to other systems.[73] In our group, these currently include functionalized cyclopentadienyls and their attachment to extended π systems, metal-complexed and not.

6. Outlook

Since our first foray into the chemistry of fulvalene dimetals,[14a] we have come a long way. The field has blossomed and the ligand has become a standard staple of the synthetic organometallic chemist. One can anticipate that with the variety of methods developed to extend fulvalene to higher oligocyclopentadienyls, these ligands may find their way into the literature with increasing frequency. Many fascinating possibilities remain to be tested, and some of them are indicated in the body of this Account. In our group, the aim will remain the uncovery of new organic reactions mediated by these assemblies, perhaps in a catalytic fashion, and the construction of novel clusters with unprecedented physical and chemical properties.

Acknowledgments

References and Notes

(1) Permanent address: Centro de Química Estrutural, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal. E-mail: cristina.azevedo@ist.utl.pt
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Graphic Abstract

---- with or without M-M bond
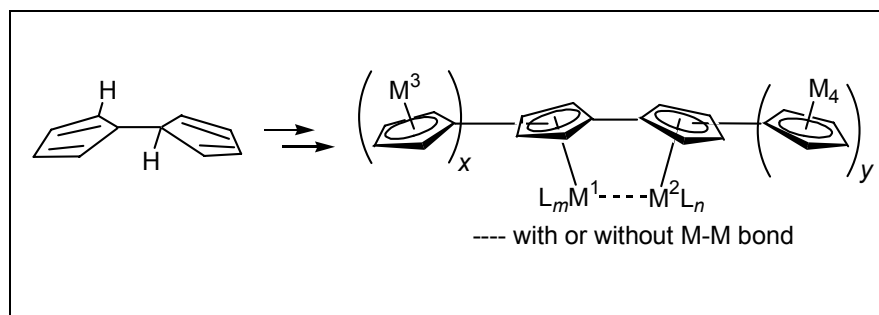
Biographical Sketches

Cristina G. de Azevedo was born in 1958 in Portugal. She studied at the Instituto Superior Técnico, Lisbon, where she graduated and received both her Msc. and Ph.D. in Chemical Engineering with Professor Carlos Romão. She carried out experimental work at the Max-Planck Institut für Kohlenforschung, Germany, in collaboration with Prof. P. W. Jolly. After a postdoctoral year at the University of California at Berkeley with Prof. K. Peter C. Vollhardt on quatercyclopentadienyl transition metal complexes, she returned to the Instituto Superior Técnico, where she is an Assistant Professor. Her research interests are organometallic chemistry, in particular the synthesis, characterization, and reactivity of group 4 and 6 transition metal complexes bearing ligands with N- and P-donor atoms.

K. Peter C. Vollhardt was born in Madrid, raised in Buenos Aires and Munich, studied at the University of Munich, got his Ph.D. with Professor Peter Garratt at the University College London, and was a postdoctoral fellow with Professor Bob Bergman (then) at the California Institute of Technology. He moved to Berkeley in 1974, when he began his efforts towards the development of organocobalt reagents in organic synthesis, the preparation of theoretically interesting hydrocarbons, the assembly of novel transition metal arrays with potential in catalysis, and the discovery of a parking space. Among other pleasant experiences, he was a Studienstiftler, Adolf Windaus medallist, Humboldt Senior Scientist, ACS Organometallic Awardee, Otto Bayer Prize Awardee, and A. C. Cope Scholar. Among his over 250 publications, he treasures especially his textbook on Organic Chemistry, translated into seven languages. He is the Chief Editor of this journal. The photograph shows him gratuitously at the center of the (extended) Thieme family of *Synlett* and *Synthesis*.

From left, 4th row: Mechthild Enders, Dieter Enders; 3rd row: Hisashi Yamamoto, Michiyo Yamamoto, Bernd Giese, Anne Giese, Thorsten Bach, Martina Otten, Laurence Harwood, Kristina Kurz, Margot Lautens, Thomas Krimmer; 2nd row: Victor Snieckus, Paul Knochel, Tohru Fukuyama, Yuri Fukuyama; 1st row: Mark Lautens, Philip Kocienski, Nathan Lautens, Peter Vollhardt, Rose Ley, Steve Ley, Susanne Haak.

Dr. Cristina G. de Azevedo